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The effluent quality of the oxygen nitrification system with pH control was excellent throughout 8 months of investigation. The effluent NH_4-N concentration averaged about 0.2 mg/l. The effluent NH_4-N of the oxygen process without pH control was normally 1 mg/l or less. However this system did not show the day-to-day stability that was achieved with pH control.

The carbonaceous and nitrogenous effluent quality of the air and oxygen nitrification systems operated at the same loadings with pH control to 7.0 in the last reactor pass of each system was identical. However three times the lime dosage was required in the oxygen system. This resulted in a larger percentage of inert material in the oxygen system and increased sludge production.

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EXPERIMENTAL EVALUATION OF OXYGEN AND AIR ACTIVATED SLUDGE NITRIFICATION SYSTEMS

With and Without pH Control

by

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

The study described in this report relates the performance of biological nitrification systems to several parameters subject to engineering control. The reliable oxidation of the ammonia present in wastewater can result in a substantial decrease in the ultimate oxygen demand exerted in the receiving aqueous environment.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

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SECTION I

INTRODUCTION

Within the past few years, the use of commercial oxygen activated sludge systems has become increasingly popular for secondary biological treatment. A logical extension of the oxygen process is its application for the biological nitrification of the ammonia present in wastewater. The nitrification process can be incorporated directly in the secondary treatment process by maintaining a sufficiently high sludge retention time (SRT) or it can be added as a separate treatment stage.

In wastewaters with a relatively low alkalinity, such as the District of Columbia, the nitric acid produced by biological nitrification results in a noticeable pH depression. This depression is intensified with gas-tight staged oxygen systems where the carbon dioxide produced by biological activity is retained as the process gas is recirculated within the stages before discharge to the atmosphere. Since the optimum pH for the nitrifying bacteria has been reported to be in the alkaline range, the pH depression may not be conducive to optimum nitrification rates.

A few preliminary studies conducted at the pilot plant suggested that the reduced pH was retarding the degree of nitrification normally encountered in systems operated at pH 7. Since these preliminary studies utilized an oxygen activated sludge system, there was also some concern that oxygen toxicity could influence the observed process performance.

The primary objectives of the study described herein were twofold:

A. To evaluate the performance of oxygen nitrification systems with and without pH control.

B. To compare the performance of oxygen and air nitrification systems operated under similar conditions.

To accomplish these objectives, three discrete biological processes were operated for varying lengths of time. Two of the processes were oxygen activated sludge systems. The pH was controlled in one of these systems but not in the other. The third biological process was an air activated sludge system operated at controlled pH. For all three systems the feed was secondary effluent from the District of Columbia biological treatment plant. Thus all systems were separate-stage nitrification reactors.

SECTION II

SUMMARY

The nitrification capabilities of two oxygen activated sludge systems receiving District of Columbia secondary effluent at a steady state flow of 190 m^3/day (50,000 gpd) were evaluated. The pH of one system was controlled to maintain a pH of 7.0 in the last reactor pass of the four pass system. The pH of the second system was uncontrolled and reactor pH values of 5.5-6.0 were common. Also parallel air and oxygen nitrification systems both with pH control were evaluated under similar operating conditions. Parameters used to compare the systems included effluent quality, sludge settling rates, lime dosage, sludge production and nitrification kinetic rates.

The effluent quality of the oxygen nitrification system with pH control was excellent throughout 8 months of investigation. The effluent NH_4-N concentration averaged about 0.2 mg/l. The effluent NH_4-N of the oxygen process without pH control was normally 1 mg/l or less. However this system did not show the day-to-day stability that was achieved with pH control.

The carbonaceous and nitrogenous effluent quality of the air and oxygen nitrification systems operated at the same loadings with pH control to 7.0 in the last reactor pass of each system was identical. However three times the lime dosage was required in the oxygen system. This resulted in a larger percentage of inert material in the oxygen system and increased sludge production. It also required maintaining higher MLSS levels to achieve the same MLVSS in each system. The improved settling characteristics of the oxygen sludge compensated for the increased solids loading to the clarifier. Both systems produced excellent effluent quality.

SECTION III

CONCLUSIONS

1. Nitrification of District of Columbia secondary effluent can be achieved in oxygen activated sludge systems with or without pH control.

2. The nitrifying organisms were estimated to comprise less than 5 per cent of the total MLSS.

3. The nitrification kinetic rates determined for the oxygen system with pH control exhibited an excellent correlation with wastewater temperature.

4. Oxygen nitrification with pH control to 7.0 in the last quarter of the reactor produced an effluent of excellent quality with an 8-month average effluent NH_4-N concentration of just 0.2 mg/l. The lime dose required to maintain the pH control was 125 mg/l as CaO.

5. The effluent NH_4-N concentration from the oxygen activated sludge process without pH control was normally 1 mg/l or less. However this system did not show the day-to-day stability that was achieved with pH control. The pH normally ranged from 5.5 to 6.0 in the last quarter of this reactor.

6. The carbonaceous and nitrogenous effluent quality from the air and oxygen activated sludge systems operated with pH control and at the same loadings were identical.

7. Because the CO_2 produced by biological activity is recirculated within the stages of the oxygen system before discharge to the atmosphere, this system required three times the lime dosage needed in the air system to maintain a pH of 7.0 in the last reactor pass.

8. During the period of parallel operation of the oxygen and air systems, the MLVSS were 36% and 58% of the MLSS, respectively. This resulted from inert material in the lime and any chemical precipitates formed in the neutralization reaction.

9. Due to the greater degree of inorganic solids produced, the MLSS in the oxygen nitrification reactor were higher than in the air nitrification system. However this produced no sludge separation problem because the sludge with the higher inert content had superior settling characteristics.

SECTION IV

RECOMMENDATIONS

It would be of interest to compare the nitrification performance of oxygen and/or air nitrification systems where the pH of one system is controlled at 7.0 and the pH of the other system is controlled at successively lower values. On the basis of the results obtained here and reported elsewhere, it appears that maintaining an acclimated system at pH 6.0 will produce nitrification rates which are equivalent to those from a system maintained at pH 7.0. There is further evidence that the nitrification rates begin to decline below pH 5.9-6.0 even for a system acclimated to lower values. The stability of the oxygen process operated at pH 6.0 should be determined. The stability of the air nitrification system without pH control should be determined. The effect of pH on nitrification at lower SRT values than those used here should be quantified. Furthermore, the trade-offs between process stability, declining nitrification kinetic rates, reduced sludge production and reduced lime dosages need to be established.

SECTION V

EXPERIMENTAL

A. Oxygen Nitrification Systems

A schematic diagram of the oxygen activated sludge process without pH control is presented in Figure 1. The reactor consisted of four passes of equal size, in series, with a total volume of 30.6 m^3 (8100 gal). The reactor was sealed to prevent loss of oxygen and included submerged hydraulic entrances and exits as well as simple water-sealed mixing equipment. Sampling ports were located at mid-depth for each reactor pass.

The addition of oxygen to the void space overlying the first pass of the reactor was controlled by a pressure regulator. The regulator activated the inlet oxygen control valve to maintain the overhead gas at a selected pressure which was maintained between 2.5-10 cm (1 to 4 inches) of water. The manual valve on the exhaust gas line was set to bleed off the exhaust gas from the void space above the fourth reactor stage at a rate sufficient to maintain an oxygen concentration of 30-50% in the exhaust line. Sample taps were installed at several locations within the system with lines leading to a Beckman oxygen analyzer for determination of the gaseous oxygen concentrations.

A series of compressors were located above each reactor pass. The gas in the overlying void space was recirculated through the compressors and down through the rotating hollow mixer shafts where it was discharged through perforated stainless steel diffusers. The diffusers were welded to the end of the mixer shafts about 30 cm (12 inches) below the impellers. The rate of gas recirculation and hence the dissolved oxygen concentrations was controlled by varying the number of compressors in use at any time and/or by the use of a control valve on the suction side of the compressors.

Mechanical energy was supplied to maintain the biological solids of each pass in the reactor in a suspended state. A single Philadelphia Gear Mixer was located directly above each pass and it was used to turn a 35 cm (14-inch) marine impeller attached to the mixer shafts.

The reactor configuration of the oxygen activated sludge system with pH control was essentially the same as shown in Figure 1. In this system, however, the influent flow and the recycle flow were mixed in a 208 l (55 gal) drum prior to entering the first pass of the reactor. A lime feeder was installed directly above the drum and dry lime was added as required to maintain a pH of 7.0 in the last reactor pass. The lime feed control strategy varied from the use of a flow proportioned feed forward - first pass pH feed back digital control program to the use of a simple timing mechanism to turn on the lime

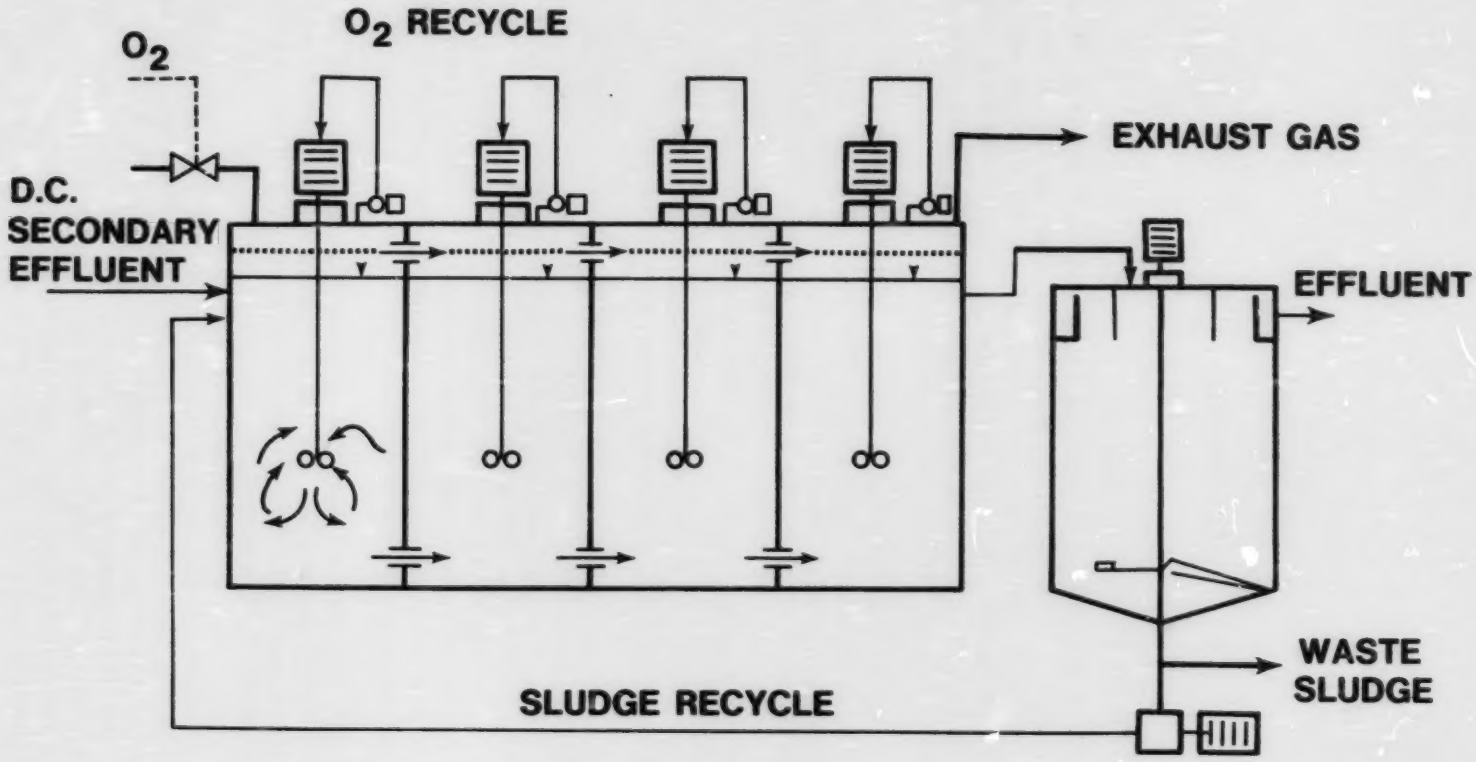

Figure 1. Oxygen Aeration System.

feeder for a preset number of seconds each minute. Because of severe and rapid slime growth on the pH electrodes, better control was obtained by the use of the simple timing mechanism.

B. Air Nitrification System

The air nitrification reactor was constructed by modifying one of the oxygen nitrification reactors. The mechanical mixers were removed and air lines were installed. These lines discharged air into PVC perforated pipe diffusers located at the bottom of each reactor pass. Removal of the mixers resulted in each pass being open to the atmosphere. This system also received dry lime for pH control. A screw feeder was located directly above the first pass of the air system, and lime was added by using a timing mechanism. Sufficient lime was added to maintain a pH of 7.0 in the last pass of the reactor.

C. Influent Flow

In all cases, the influent flow consisted of District of Columbia secondary effluent obtained from the effluent channel of the 762 m^3/min (290 mgd) D.C. Blue Plains Wastewater Treatment Plant. The flow rate was maintained near 132 l/min (35 gpm) at all times providing a daily flow of about 191 m^3/day (50,400 gpd). The flow passed through a magnetic flow meter and the actual flow was recorded once per day from a flow totalizer attached to the magnetic flow meter. A pneumatically controlled valve in the influent feed line to each system was adjusted as required to maintain the flow at the desired rate.

D. Biological System Clarifiers

The discharge from either the air or oxygen nitrification systems flowed to center-feed clarifiers with surface areas of 7.2 m^2 (78 ft^2). This provided for an overflow rate of 26.3 m/day (645 gpd/ft^2) at the steady 132 l/min (35 gpm) flow. The recycle flow rate was varied as operating conditions warranted.

SECTION VI

METHODS AND PROCEDURES

Each process was monitored on a 24-hour a day, 7-day a week schedule. The only interruptions in the normal operating sequence resulted from mechanical difficulties and necessary repairs were always made within a short time. Grab samples of reactor influent and clarified effluent were taken every four hours, and grab samples of mixed liquor and recycle solids were obtained every eight hours for the laboratory analyses described below. The grab samples were composited over a 24-hour period on Tuesday, Wednesday and Thursday; samples collected on Friday-Saturday and on Sunday-Monday were composited over the 48-hour period. The single exception to this was that the samples for BOD_5 measurement were always 24-hour composites and the analysis was always started within a few hours (4-10 hours) after the last sample for each 24-hour composite had been collected. All samples were refrigerated at 2°C prior to analysis. In addition, all samples except those taken for BOD_5 or suspended solids analysis were preserved with one drop of H_2SO_4 per 30 ml of sample while they were being held in storage. All laboratory analyses (except BOD_5) were performed on a Monday through Friday schedule.

The following analyses were performed in the District of Columbia Pilot Plant laboratories according to the procedures specified in Standard Methods (1): suspended solids, volatile suspended solids, BOD_5, COD and TKN. Also, BOD_5 analyses were performed with nitrate production inhibited by the addition of 0.5 mg/l of allylthiourea (2). The procedures specified in the EPA Manual (3) were used for the determination of NH_4-N, NO_3-N and NO_2-N with a Technicon autoanalyzer. The method of Gales et al. (4) was used for the determination of total phosphorus. Calcium concentrations were measured by atomic absorption with a Perkin-Elmer Model 303 Spectrometer.

In addition to collecting grab samples and compositing them for subsequent laboratory analysis, the operating personnel also: (a) checked the mixed liquor dissolved oxygen levels in the appropriate reactors every four hours and adjusted the oxygen recirculation rates or air flow rates as necessary to keep a D.O. of 5-12 mg/l in the oxygen systems and 2-4 mg/l in the air nitrification system; (b) obtained solids samples for 30-minute sludge volume determinations in one-liter cylinders; (c) measured temperature, pH and alkalinity of selected samples; (d) measured the depth of the sludge blankets in the clarifiers; and (e) adjusted the lime feed rates if needed.

Sludge wasting was done manually by diverting the sludge recycle flow to a calibrated drum. When the waste rate was 0.19 m^3/day (50 gpd) or less, the wasting was done once per day. For waste rates in excess of 0.19 m^3/day (50 gpd), wasting of approximately equal increments was done twice per day.

Throughout the year, samples of mixed liquor were removed periodically and settling tests were run in 2.3 m x 0.15 m (7.5 ft x 6 inches) diameter stirred columns. The stirring mechanism consisted of two 0.64 cm (1/4 inch) diameter rods which extended the length of the column and rotated around the vertical axis at a rate of 10-14 rph. Settling rates in which the recycle solids were mixed in varying proportions with process effluent were also occasionally evaluated.

On numerous occasions, batch kinetic studies were undertaken in the laboratory to determine nitrification kinetic rates. The nitrification studies were performed by mixing 1-2 liters of recycle solids with District of Columbia secondary effluent. A water bath was normally employed to insure that the temperature of the kinetic analysis remained the same as that which existed in the process. For those systems where pH control was practiced, the initial pH in the kinetic study was adjusted with lime to a value similar to that existing in the first pass of the process under investigation. Special studies in which the pH was controlled at some constant value during the kinetic test were also performed. During the kinetic test the sludge from the oxygen systems was aerated with pure oxygen with sufficient mechanical stirring supplied with a magnetic stirer and stirring bar to maintain the solids in suspension. The D.O. was maintained between 5 and 12 mg/l. Diffused air was added to the air nitrification sludge and the D.O. was maintained between 2 and 4 mg/l. The decrease in NH_4-N was monitored by automated analysis. In all cases, the NH_4-N removal followed zero order kinetics until the exogenous NH_4-N levels dropped to near 1 mg/l.

The kinetic rates were always expressed per unit of MLVSS. In some cases, the rates were also expressed per unit of sludge protein or per unit of sludge ATP. Sludge protein was estimated by the Folin procedure (5). Interferences by non-proteinaceous material are common with this procedure (6), but this was not of concern for the purposes of this study. Biological solids were disrupted on a Bronson Sonifier prior to analysis. Sludge ATP was extracted by boiling the cells for five minutes in tris buffer, and the concentrations were measured in a Biospherics Biometer. Samples for protein and ATP were frozen immediately after collection and maintained in this state until the analyses were performed. The MLVSS determinations were always performed immediately after the kinetic test.

Dissolved oxygen uptake rates were periodically measured by withdrawing a sample of mixed liquor from the reactor pass of interest and immediately measuring the decrease in dissolved oxygen as a function of time. The studies were performed in mechanically stirred BOD_5 bottles with a Delta Scientific D.O. probe inserted into the tapered bottle neck.

SECTION VII

RESULTS

A. Introduction

The oxygen activated sludge system with no pH control was placed on stream at the end of September 1973 and operated until the later part of May 1974. The original research plan called for running the pH controlled oxygen activated sludge system during the same time period. However this system was not started until January 1974 because of delays in procuring needed equipment. In view of this period of nonoverlapping operation, the results from the oxygen activated sludge studies will be presented in two discrete phases. The first phase covers the results obtained when just the oxygen activated sludge system with no pH control was in operation; this period extends from October thru December 1973. The second phase of operation presented covers the period when both oxygen nitrification systems were in operation (January thru May 1974). A third phase of operation will be presented which covers the period when the oxygen and air nitrification systems were being compared. These results were obtained from June thru September 1974 and are summarized under Phase III.

B. Phase I (October-December 1973):

A step-feed oxygen activated sludge system receiving D.C. primary effluent at the rate of 379 m^3/day (100,000 gpd) was operated at the pilot plant during the Fall of 1973. On September 28 (day 271) the system was temporarily shut down and reconverted to an oxygen aeration system receiving D.C. secondary effluent as illustrated in Figure 1. Sufficient nitrifying organisms were present in the sludge to produce immediate complete nitrification.

The variation in mixed liquor solids and effluent TKN and NH_4-N from the oxygen aeration system is presented in Figure 2. The data points shown represent 5-day averages. There was no deliberate wasting from the system during October. However, the change in influent wastewater from primary to secondary effluent was accompanied by a gradual decline in mixed liquor solids until the latter part of the month. From days 302-316 there was repeated failure of the influent flow controller resulting from the inadvertent cross-connection of pneumatic and hydraulic control lines. This resulted in extreme flow variations and the effluent quality during this period is not amenable to meaningful analysis. From days 317-351, the process ran under stable influent flow and with a constant volumetric waste rate. As shown in Figure 2, there was a gradual rise in effluent NH4-N during this period. The increased effluent NH_4-N corresponds to reduced nitrification kinetic rates resulting from the decline in wastewater temperature as shown in Figure 3.

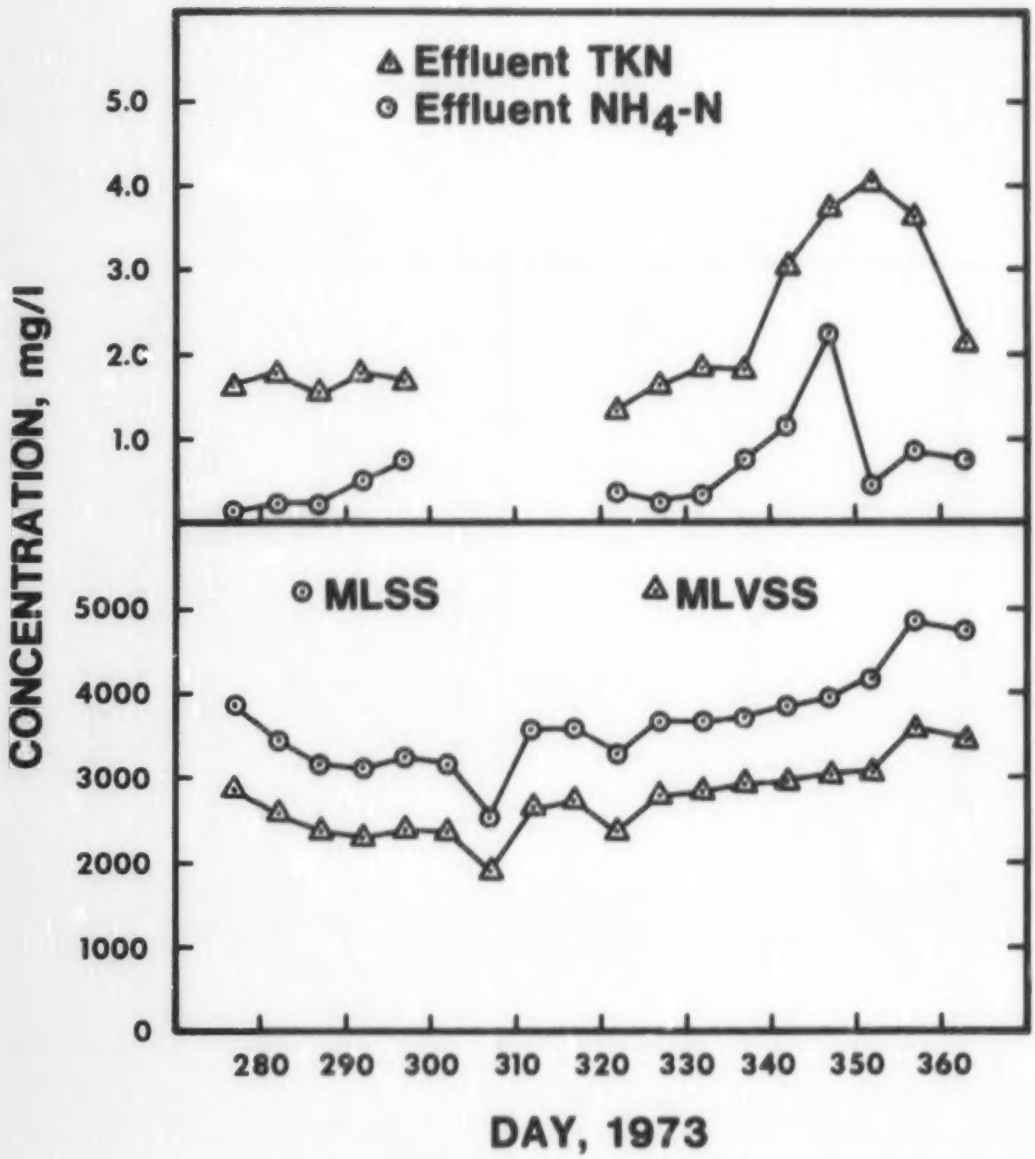

Figure 2. Reactor Solids and Effluent Nitrogen for the Oxygen Nitrification System Without pH Control (Days 275-365, 1973).

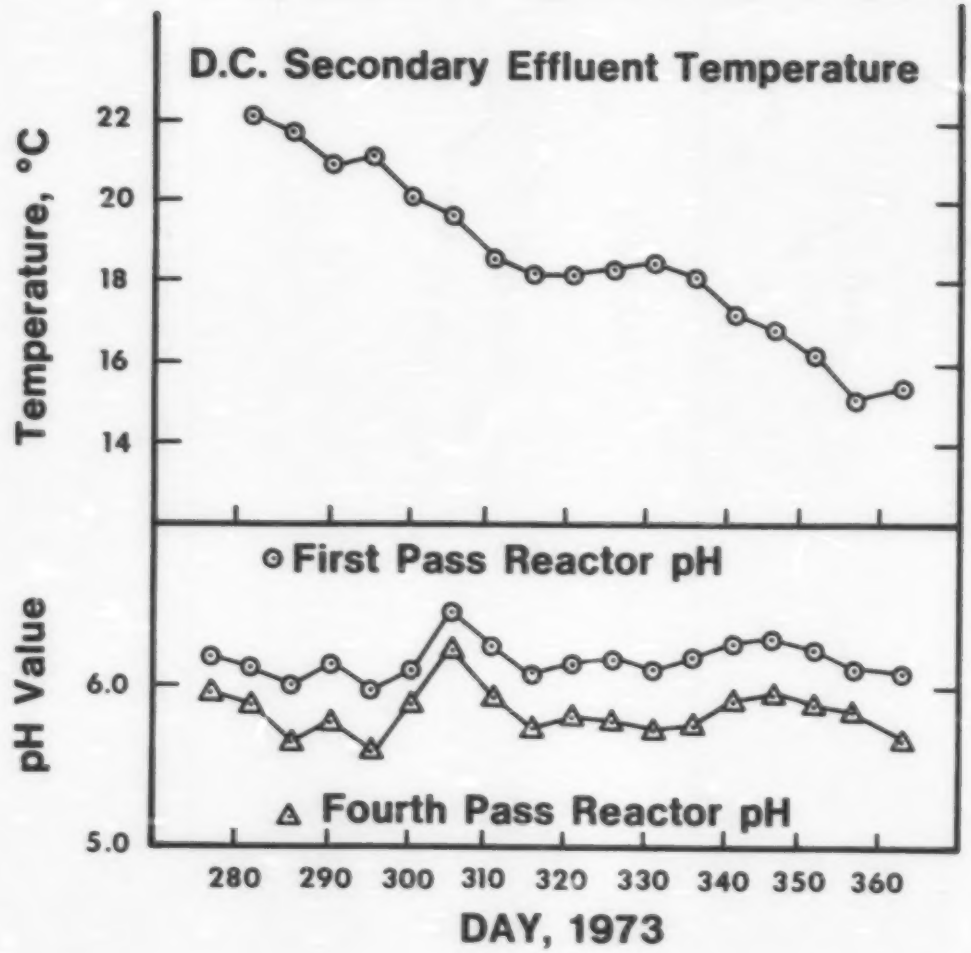

Figure 3. D.C. Secondary Effluent Temperature and Reactor pH for the Oxygen Nitrification System Without pH Control (Days 275-365, 1973).

Results obtained from the operation during days 317-351 are summarized in Tables 1 and 2. It can be seen that the District of Columbia secondary effluent, which serves as the influent to the oxygen nitrification process, is of poor quality with an average BOD_5 of 61 mg/l and a COD of 141 mg/l. To a large extent this poor quality results from hydraulic overload of the secondary clarifiers resulting in a relatively high suspended solids in the effluent. No nitrification occurs in the D.C. secondary treatment process.

Flow to the oxygen nitrification system averaged 186 m^3/day (49,100 gpd) for a corresponding detention time of 3.9 hours. The volumetric waste rate was maintained at a constant value. The resulting SRT (7) was approximately 28 days. As indicated in Figure 3, the reactor pH during this period dropped to around 5.7 in the fourth reactor pass. The pH data shown represent the median pH values for each 5-day period. The last pass reactor pH frequently reached pH 5.5 and there were a few occasions when it was reduced to 5.3.

The clarifier blanket rose slowly during the month of December and by day 352 it was necessary to reduce the flow to maintain the blanket within the clarifier. During the last 14 days of the year (days 351-365) the flow was stable and averaged 156.7 m^3/day (41,400 gpd) with a reactor detention time of 4.7 hours. This reduced the clarifier overflow rate to 21.6 m/day (530 gpd/ft^2). The additional detention time and the possibility of increased acclimation to the colder temperature resulted in a reduction of the residual effluent NH_4-N concentration to less than 1 mg/l.

C. Phase II (January-May 1974)

On the second of January, the flow to the oxygen nitrification system was increased to 191 m^3/day (50,400 gpd). This did not produce any problems with the clarifier blanket level which remained 0.9-1.5 m (3-5 ft) below the clarifier surface. On both the 7th and 8th of January, 1.9 m^3 (500 gal) of recycle solids were removed from the oxygen system and used to seed the oxygen nitrification system with pH control. The removal of 3.8 m^3 (1000 gal) of solids, which was 17 times the normal volumetric wasting, resulted in a temporary increase in effluent NH_4-N (Figure 4, day 10). However the system recovered rapidly and the solids levels and residual NH_4-N levels returned to their previous levels by the last third of the month.

Flow to the oxygen nitrification system with pH control was at steady state and averaged 185 m^3/day (48,900 gpd) during the last half of January. By the end of the month the MLSS concentration had increased to 5000 mg/l and at this time the full sampling sequence for laboratory analysis was initiated.

The variations in effluent TKN and NH_4-N, MLSS, MLVSS and temperature and pH for both oxygen systems are shown in Figures 4 thru 7, respectively. The data points shown represent five-day averages. As shown in Figure 6, the MLVSS concentration in the system with pH control remained reasonably constant from days 51-150. The operational characteristics of the system during this 100-day time period and the influent and effluent quality are summarized in Tables 3 and 4, respectively. The effluent NH_4-N concentration was extremely low and exhibited only a small daily variation. Other effluent parameters eg. COD and

TABLE 1. PROCESS CHARACTERISTICS FOR THE OXYGEN NITRIFICATION SYSTEM WITHOUT pH CONTROL (DAYS 317-351, 1973)

	Value or Average	Standard Deviation	Standard Error
Influent Flow, m^3/day	186		
Influent Flow, gpd	49,100		
Aeration Time, hours	3.9		
Clarifier Overflow Rate, m/day	25.6		
Clarifier Overflow Rate, gpd/ft^2	630		
MLSS, mg/l	3690	386	47.5
MLVSS, mg/l	2790	298	36.7
Recycle SS, mg/l	15,400	1493	252
Recycle VSS, mg/l	11,725	1125	190
Recycle TKN, mg/l	1148	140	23.9
Recycle COD, mg/l	17,250	1630	284
SRT, days	28		
F/M Ratio, Kg BOD_5/day/Kg MLVSS	0.13		
Total Solids Production, mg/l	22.8		
Total Solids Production, lb/MG	190		
Percent of Solids Production in Effluent, %	57.9		

TABLE 2. INFLUENT AND EFFLUENT CHARACTERISTICS FOR THE OXYGEN NITRIFICATION SYSTEM WITHOUT pH CONTROL (DAYS 317-351, 1973)

	Influent, mg/l			Effluent, mg/l		
	Mean	Standard Deviation	Standard Error	Mean	Standard Deviation	Standard Error
BOD_5	61	12.1	2.1	13.5	4.3	0.7
Inhibited BOD_5	--			6.8	2.7	0.5
COD	141	19.3	3.4	30.6	7.1	1.2
SS	64	16.3	3.0	13	6.9	1.2
VSS	49	13.0	2.4	9	5.3	0.9
TKN	22.0	1.9	0.3	2.5	1.5	0.3
NH_4-N	16.5	1.0	0.2	1.1	1.2	0.2
$(NO_2 + NO_3)$-N	--			11.4	1.7	0.3
Alkalinity*	129	13.8	1.4	42	7.5	0.7
Ca^{++}	35.7	3.8	0.7	34.8	3.4	0.6

* As $CaCO_3$

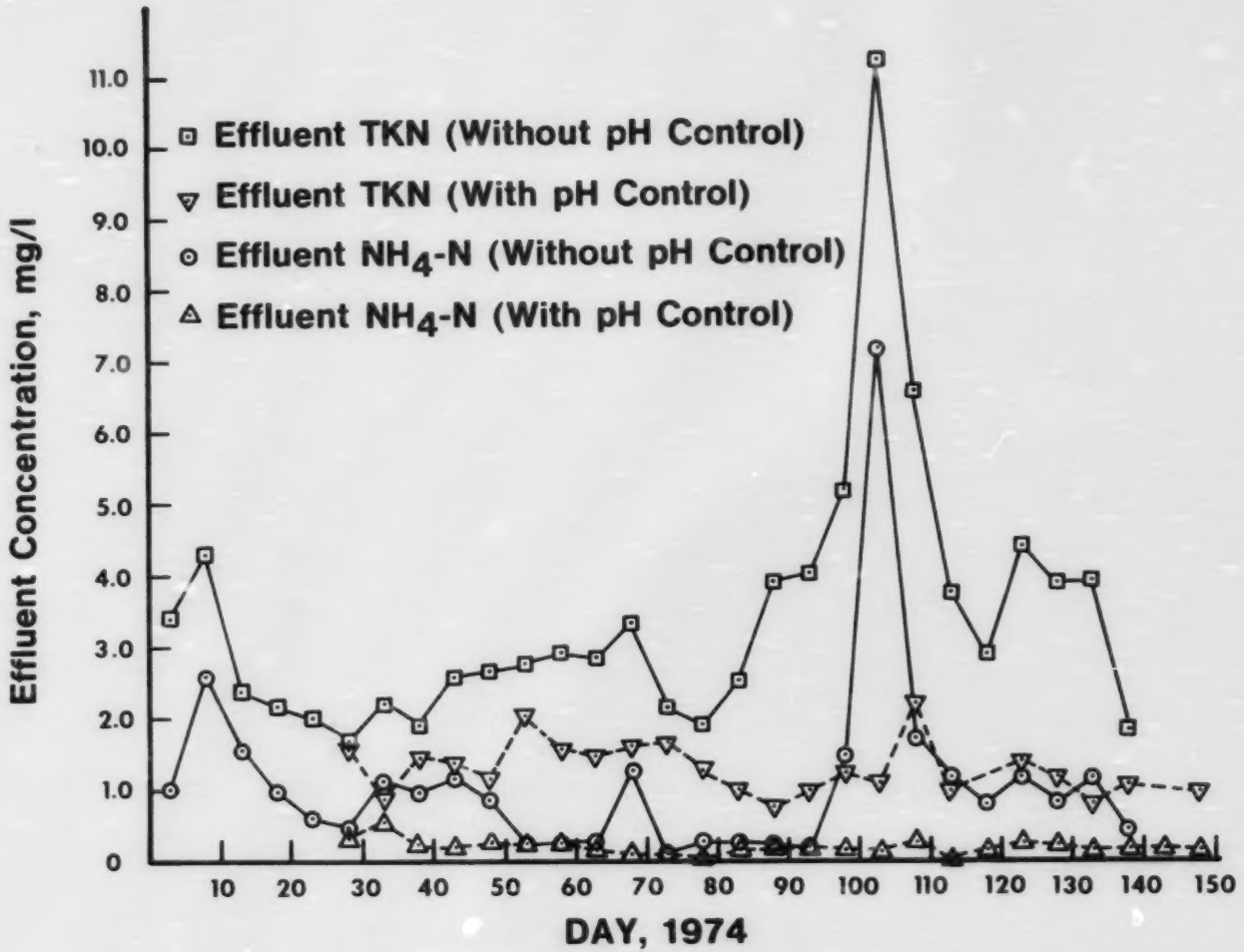

Figure 4. Effluent TKN and NH_4-N for the Oxygen Nitrification Systems With and Without pH Control (Days 1-150, 1974).

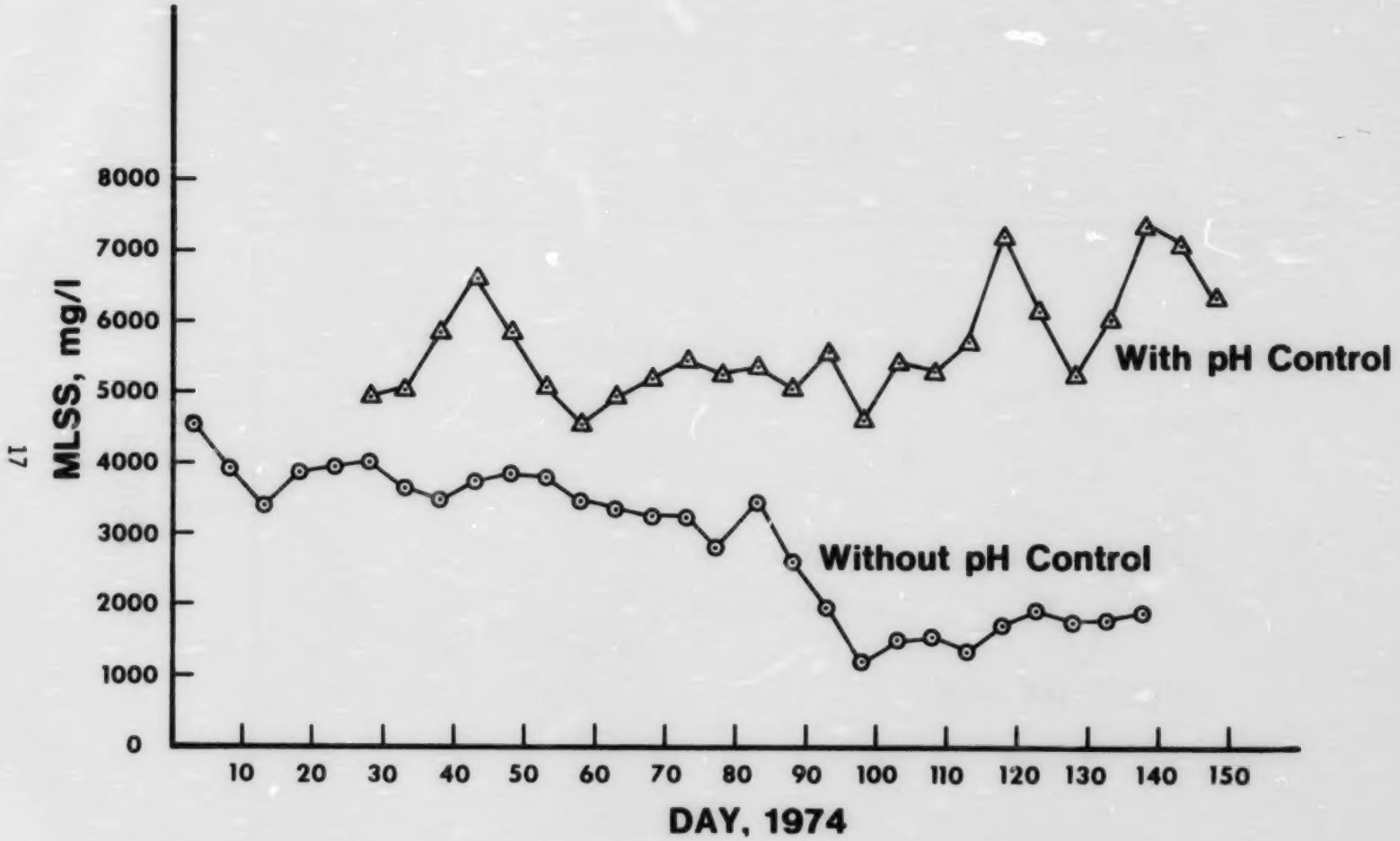

Figure 5. Reactor MLSS Concentrations for the Oxygen Nitrification Systems With and Without pH Control (Days 1-150, 1974).

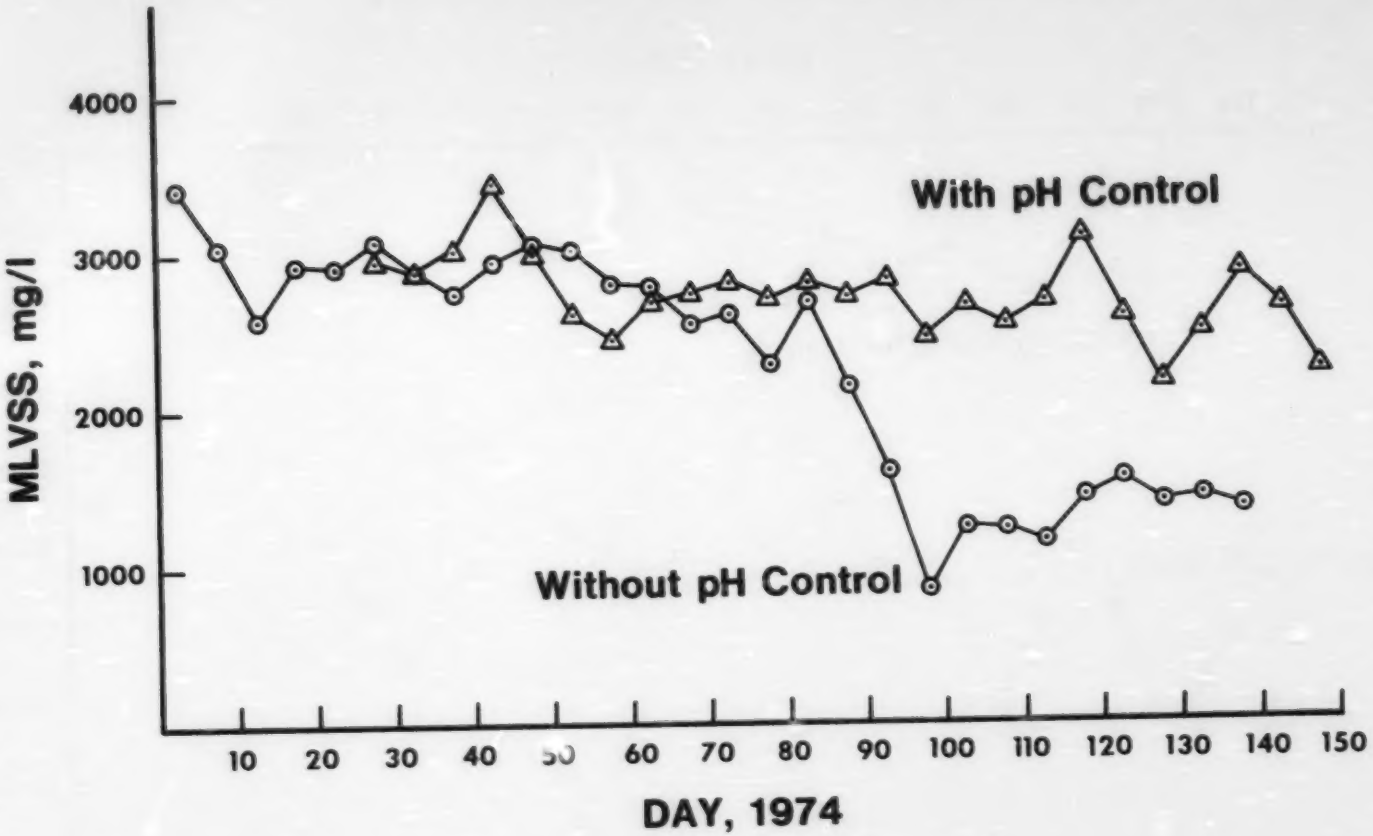

Figure 6. Reactor MLVSS Concentrations for the Oxygen Nitrification Systems With and Without pH Control (Days 1-150, 1974).

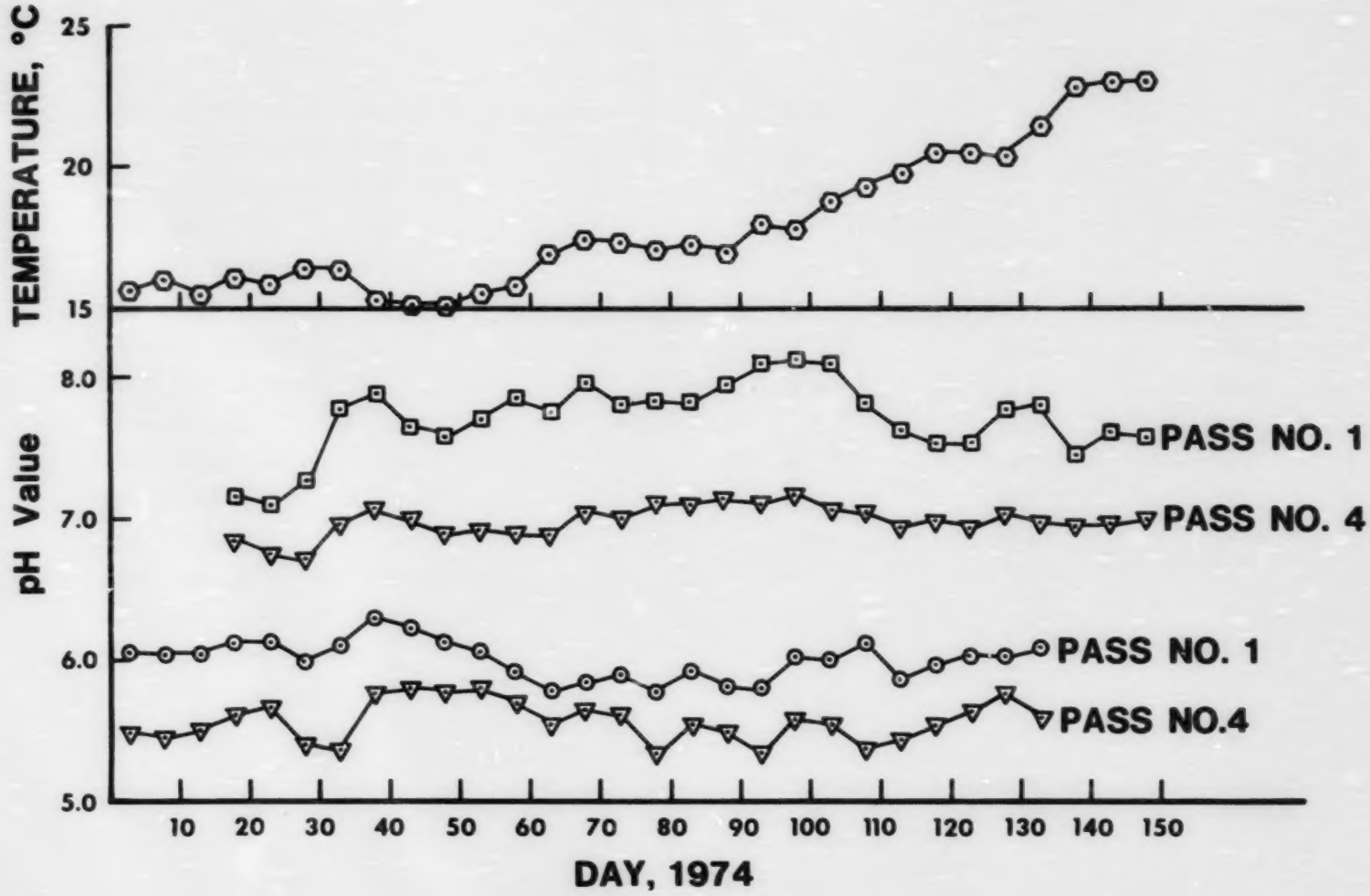

Figure 7. D.C. Secondary Effluent Temperature and Reactor pH Values for the Oxygen Nitrification Systems With and Without pH Control (Days 1-150, 1974).

TABLE 3. PROCESS CHARACTERISTICS FOR THE OXYGEN NITRIFICATION SYSTEM WITH pH CONTROL (DAYS 51-150, 1974)

	Value or Average	Standard Deviation	Standard Error
Influent Flow, m^3/day	183.2		
Influent Flow, gpd	48,400		
Aeration Time, hours	4.0		
Clarifier Overflow Rate, m/day	25.3		
Clarifier Overflow Rate, gpd/ft^2	620		
MLSS, mg/l	5660	928	67.3
MLVSS, mg/l	2620	288	21.1
Recycle SS, mg/l	38,650	4316	443
Recycle VSS, mg/l	18,150	2250	236
Recycle TKN, mg/l	1710	251	26.9
Recycle COD, mg/l	24,920	3580	380
SRT, days	13		
F/M Ratio, Kg BOD_5/day/Kg MLVSS	0.15		
Lime Dose, mg/l	126		
Total Solids Production, mg/l	69.0		
Total Solids Production, lb/MG	575		
Percent of Solids Production in Effluent, %	14.5		

TABLE 4. INFLUENT AND EFFLUENT CHARACTERISTICS FOR THE OXYGEN NITRIFICATION SYSTEM WITH pH CONTROL (DAYS 51-150, 1974)

	Influent, mg/l			Effluent, mg/l		
	Mean	Standard Deviation	Standard Error	Mean	Standard Deviation	Standard Error
BOD_5	67	12.7	1.3	14.3	5.3	0.55
Inhibited BOD_5	--			6.3	3.1	0.33
COD	152	20.9	2.2	26.4	6.2	0.63
SS	77	21.4	2.3	10.0	4.8	0.53
VSS	58	16.7	1.8	6.0	4.2	0.46
TKN	21.7	2.4	0.26	1.3	0.55	0.06
NH_4-N	14.9	2.0	0.20	0.15	0.11	0.01
$(NO_2 + NO_3)$-N	--			13.4	1.1	0.11
Phosphorus **	6.2	0.85	0.09	3.6	0.68	0.08
Ca^{++}	29.5	4.4	0.47	82.3	7.0	0.76

** Days 60-150

SS were also quite low and indicate that the oxygen process with pH control reliably produces a high quality effluent. Average values in March and May are compared in Table 5 to illustrate the increased carbonaceous effluent quality which was obtained during the warmer weather. The reduced concentration of suspended solids in the effluent, in all likelihood, represented an increase in clarification efficiency resulting from the warmer wastewater. To maintain a pH of 7.0 in the last pass of the reactor required an average lime dose of 126 mg/l of Warner High Ca Lime (8). The inert materials contributed by the lime required that higher MLSS concentrations be maintained as compared to the system with no pH control in order to maintain the same level of reactor MLVSS.

On day 86 and on one and possibly two occasions thereafter there were large inadvertent solids losses from the oxygen nitrification system without pH control because of a malfunctioning valve. These solids losses produced a large decrease in reactor solids and the large temporary increase in the effluent NH_4-N concentration shown in Figure 4. This solids loss limits the time period for which a meaningful direct comparison of the two oxygen systems can be made to days 56-85, a period of 30 days. During this period the MLVSS in the system without pH control averaged 2620 mg/l (Standard Deviation = 241) compared to an average of 2690 mg/l (Standard Deviation = 199) in the system with pH control. As shown in Table 6, the system with pH control provides an effluent of somewhat better quality. The better carbonaceous quality can be explained by an increase in clarification efficiency resulting from the high lime dosage. The residual NH_4-N level is also somewhat lower with pH control but the difference is small. The pH adjustment results in a 50 mg/l increase of calcium ion.

The operating characteristics of the system without pH control have been summarized for the 60 day period of days 26-85 (Tables 7 and 8). The operating characteristics from days 115-141 have also been summarized (Tables 9 and 10). In this case, however, the time period was insufficient to insure that equilibrium operation existed. For this reason, the SRT has not been determined. Nonetheless, the results indicate that the process performed well (average effluent NH_4-N <1.0 mg/l) at the low reactor solids levels.

D. Phase III (June-September 1974)

On the 148th day of the year (May 28), the recycle pump to the oxygen nitrification system without pH control was turned off while leaving the influent flow on. The mixing equipment was removed during the morning of day 149, the reactor was drained, and diffusors for compressed air aeration were installed. Also a dry lime feeder was installed to feed lime directly into the first pass of the reactor. The unit was placed on stream by the afternoon of day 149 at a flow of 132 l/min (35 gpm). The amount of solids saved in the clarifier during system modification was insufficient. Consequently, 1.5 m^3 (400 gal) of recycle solids from the oxygen nitrification system with pH control were added to the air system on day 154. This produced reactor solids of 3000 mg/l and resulted in a completely nitrified effluent by day 156.

The removal of the 1.5 m^3 (400 gal) of recycle solids from the oxygen system

TABLE 5. EFFLUENT CHARACTERISTICS OF THE OXYGEN NITRIFICATION SYSTEM WITH pH CONTROL FOR MARCH AND MAY 1974

	March mg/l			May mg/l		
	Mean	Standard Deviation	Standard Error	Mean	Standard Deviation	Standard Error
BOD_5	18.5	4.0	0.7	10.0	3.9	0.7
Inhibited BOD_5	8.5	2.9	0.5	4.0	1.5	0.3
COD	30.0	5.4	1.0	22.1	3.2	0.6
TKN	1.3	0.51	0.1	1.1	0.44	0.1
NH_4-N	0.12	0.11	0.02	0.18	0.07	0.01
$(NO_2 + NO_3)$-N	13.1	0.80	0.2	14.3	0.96	0.2
Phosphorus	3.6	0.9	0.2	3.8	0.6	0.1
SS	13	5.1	1.1	7	3.7	0.7
VSS	9	5.2	1.1	3	1.6	0.3
Ca^{++}	82.1	7.1	1.4	81.2	5.5	1.1

TABLE 6. INFLUENT AND EFFLUENT CHARACTERISTICS FOR THE OXYGEN NITRIFICATION SYSTEMS WITH AND WITHOUT pH CONTROL (DAYS 56-85, 1974)

	Influent, mg/l			Effluent, mg/l With pH Control			Effluent, mg/l Without pH Control		
	Mean	Standard Deviation	Standard Error	Mean	Standard Deviation	Standard Error	Mean	Standard Deviation	Standard Error
BOD_5	74	11.2	2.1	18.9	3.9	0.7	21.2	4.2	0.8
Inhibited BOD_5	--			8.7	2.8	0.5	9.4	2.7	0.5
COD	161	17.6	3.3	31.0	4.8	0.9	45.4	6.3	1.2
SS	84	24.3	4.6	12	5.1	1.0	26	12.2	2.4
VSS	67	17.4	3.3	9	5.2	1.1	20	10.2	2.0
TKN	23.0	1.9	0.4	1.4	0.45	0.09	2.6	0.71	0.14
NH_4-N	14.0	1.4	0.3	0.11	0.10	0.02	0.42	0.53	0.11
$(NO_2 + NO_3)$-N	--			13.2	0.7	0.14	13.3	0.90	0.18
Phosphorus**	6.7	1.1	0.2	3.8	0.8	0.2	4.9	0.5	0.1
Ca^{++}	31.3	2.7	0.5	82.6	6.4	1.2	30.6	2.8	0.5

** Days 60-85

TABLE 7. PROCESS CHARACTERISTICS FOR THE OXYGEN NITRIFICATION SYSTEM WITHOUT pH CONTROL (DAYS 26-85, 1974)

	Value or Average	Standard Deviation	Standard Error
Influent Flow, m^3/day	190		
Influent Flow, gpd	50,300		
Aeration Time, hours	3.9		
Clarifier Overflow Rate, m/day	26.3		
Clarifier Overflow Rate, gpd/ft^2	645		
MLSS, mg/l	3520	379	36.2
MLVSS, mg/l	2780	290	27.4
Recycle SS, mg/l	13,640	1380	186
Recycle VSS, mg/l	10,780	1160	155
Recycle TKN, mg/l	1120	173	23.1
Recycle COD, mg/l	16,170	1974	261
SRT, days	17		
F/M Ratio, Kg BOD_5/day/Kg MLVSS	0.16		
Total Solids Production, mg/l	35.4		
Total Solids Production, lb/MG	295		
Percent of Solids Production in Effluent, %	68		

TABLE 8. INFLUENT AND EFFLUENT CHARACTERISTICS FOR THE OXYGEN NITRIFICATION SYSTEM WITHOUT pH CONTROL (DAYS 26-85, 1974)

	Influent, mg/l			Effluent, mg/l		
	Mean	Standard Deviation	Standard Error	Mean	Standard Deviation	Standard Error
BOD_5	70	12.6	1.7	20.4	4.4	0.6
Inhibited BOD_5	--			8.6	3.0	0.4
COD	152	21.9	3.2	42.5	8.2	1.1
SS	75	24.7	3.4	24.0	10.2	1.5
VSS	58	19.6	2.7	17.1	8.6	1.2
TKN	22.7	2.0	0.3	2.4	0.68	0.09
NH_4-N	15.0	1.8	0.25	0.64	0.64	0.09
$(NO_2 + NO_3)$-N	--			12.8	1.2	0.2
Alkalinity (1)	130	11.1	1.4	31	8.9	1.2
Ca^{++} (2)	33	5.0	0.7	32	4.6	0.7

(1) As $CaCO_3$

(2) Days 32-85, 1974

TABLE 9. PROCESS CHARACTERISTICS FOR THE OXYGEN NITRIFICATION SYSTEM WITHOUT pH CONTROL (DAYS 115-141, 1974)

	Value or Average	Standard Deviation	Standard Error
Influent Flow, m^3/day	189		
Influent Flow, gpd	49,900		
Aeration Time, hours	3.9		
Clarifier Overflow Rate, m/day	26.1		
Clarifier Overflow Rate, gpd/ft^2	640		
MLSS, mg/l	1820	187	26.5
MLVSS, mg/l	1420	123	17.4
Recycle SS, mg/l	6335	650	139
Recycle VSS, mg/l	4915	546	116
Recycle TKN, mg/l	501	63.8	13.6
Recycle COD, mg/l	7005	752	160
F/M Ratio, Kg BOD_5/day/Kg MLVSS	0.30		

TABLE 10. INFLUENT AND EFFLUENT CHARACTERISTICS FOR THE OXYGEN NITRIFICATION SYSTEM WITHOUT pH CONTROL (DAYS 115-141, 1974)

	Influent, mg/l			Effluent, mg/l		
	Mean	Standard Deviation	Standard Error	Mean	Standard Deviation	Standard Error
BOD_5	68	11.5	2.3	27.2	6.0	1.2
Inhibited BOD_5	--			13.7	3.7	0.8
COD	153	25.1	4.9	58	7.0	1.4
SS	79	15.8	3.1	27.5	7.6	1.5
VSS	59	14.5	2.9	18.4	4.8	1.0
TKN	21.8	2.3	0.5	3.3	1.1	0.2
NH_4-N	16.6	1.6	0.3	0.83	0.45	0.09
$(NO_2 + NO_3)$-N	--			15.1	1.0	0.2
Phosphorus	6.2	0.7	0.1	5.3	0.4	0.1
Alkalinity *	133	6.5	1.2	31	8.2	1.6
Ca^{++}	29	3.6	0.8	29	3.4	0.7

* As $CaCO_3$

had no noticeable impact on product quality. The effluent COD for the month of June averaged 19.7 mg/l and the NH_4-N level was 0.19 mg/l.

The MLSS and MLVSS levels in the air and oxygen nitrification systems are shown in Figure 8. It can be seen that the MLVSS levels were generally within 10 per cent of each other. This is not true of the MLSS concentrations because of the difference in lime requirement to maintain pH 7.0 in the last pass.

The process characteristics for each of the two systems for the 80 day period from days 186-265 are summarized in Tables 11 and 12. The carbonaceous effluent quality and the residual NH_4-N and TKN levels are the same (Figure 9). The increased phosphorus removal in the oxygen system relative to the air system apparently results from the higher lime dosage needed to maintain a fourth pass reactor pH of 7.0 in the oxygen system. As shown in Figure 10, the fourth pass reactor pH values were essentially identical in both systems but there was a larger pH drop across the four passes of the oxygen system than occurred in the air system. The higher pH in the first pass of the oxygen system compared to the air system produced the increased phosphate precipitation.

The average SRT values for the 80 day period summarized in Table 11 were essentially the same. During July, August and September, the respective SRT values for the air and oxygen systems were 11.1 and 12.2; 10.5 and 11.7; and 7.9 and 6.5 days. The lower SRT values in September reflect the increased wasting which was applied to the system during the last month of operation. Sufficient time was not available to characterize these two systems under extended equilibrium operation at these relatively low SRT's.

The only drawback to the air nitrification system was the poorer settling properties of its sludge compared to the oxygen system. The average SVI for the air system from days 186-265 was 194 ml/gm whereas it was only 55 ml/gm for the oxygen system. Results of batch settling tests in the 0.15 m (6 inch) diameter column over a range of solids concentrations are presented in Figure 11. The increased settling velocities in the oxygen system more than compensated for the increase in MLSS which were carried in this system to maintain the same MLVSS level as in the air system. As previously indicated the difference in the percent volatile solids reflects inert material resulting from the differing lime dosages for pH control.

E. Supplemental Studies and Analyses

Throughout the course of the study, nitrification kinetic rates were determined by laboratory batch kinetic studies. Although the interpretation of kinetic values can be misleading (see Discussion), it is felt that these studies provided a useful tool for comparison of the various processes. The results obtained from all kinetic evaluations are presented in Tables 13 thru 18. In all cases the laboratory studies yielded zero order kinetic constants. The results of a typical kinetic analyses are presented in Figure 12.

As shown in Table 14, the laboratory kinetic rates in the system without pH control were consistently somewhat higher than in the pH controlled system on

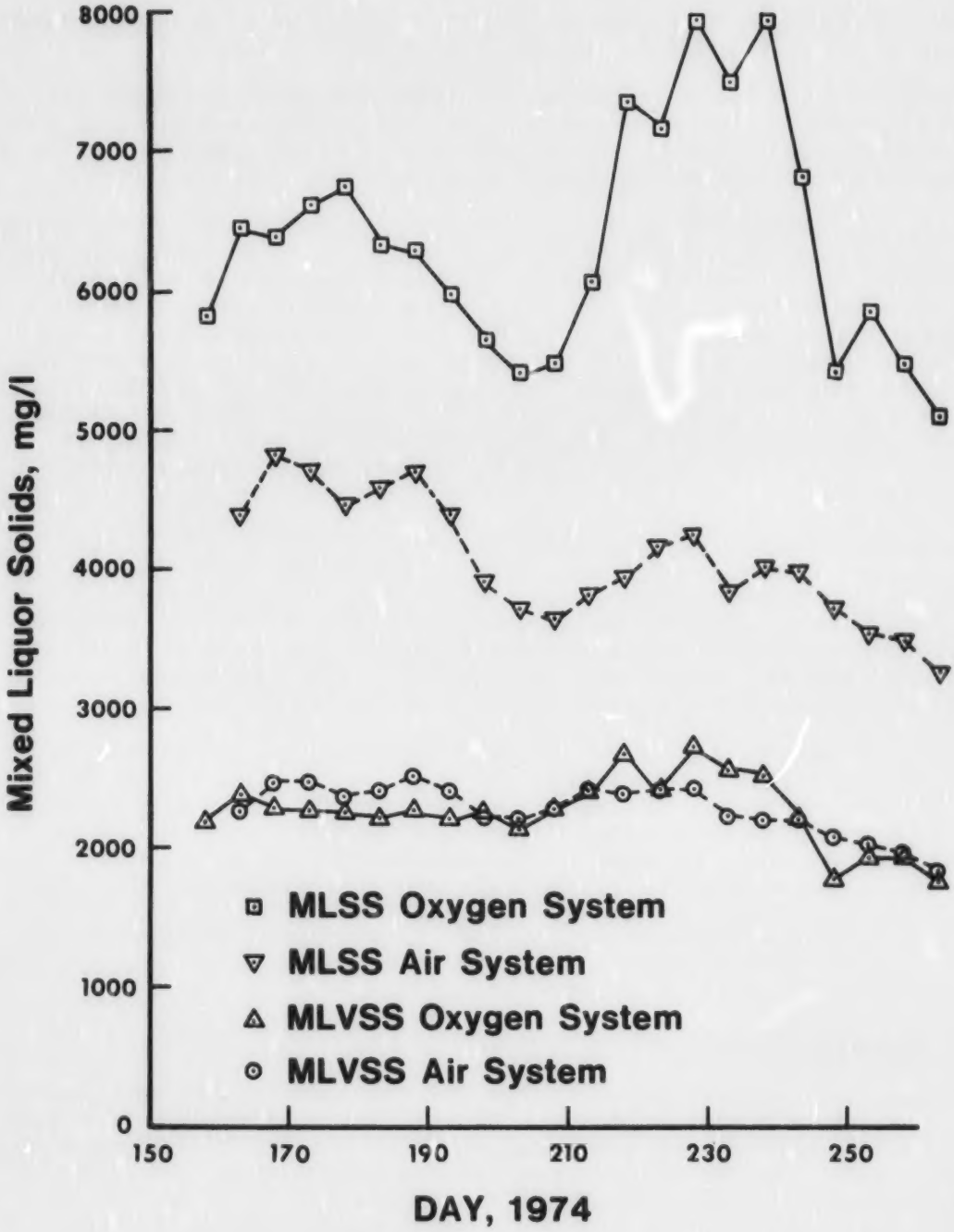

Figure 8. Reactor MLSS and MLVSS Concentrations in the Air and Oxygen Nitrification Systems (Days 155-265, 1974).

TABLE 11. PROCESS CHARACTERISTICS FOR THE AIR AND OXYGEN NITRIFICATION SYSTEMS WITH pH CONTROL (DAYS 186-265, 1974)

	Air System		Oxygen System	
	Value or Average	Standard Deviation	Value or Average	Standard Deviation
Influent Flow, m^3/day	200.2		193.8	
Influent Flow, gpd	52,900		51,200	
Aeration Time, hours	3.7		3.8	
Clarifier Overflow Rate, m/day	27.6		26.7	
Clarifier Overflow Rate, gpd/ft^2	678		656	
MLSS, mg/l	3890	397	6355	1094
MLVSS, mg/l	2240	215	2260	359
Recycle SS, mg/l	16,460	1610	40,850	6860
Recycle VSS, mg/l	9460	982	14,040	1460
Recycle TKN, mg/l	929	94	1270	165
Recycle COD, mg/l	13,050	1330	18,240	2255
SRT, days	9.9		10.0	
F/M Ratio, Kg BOD_5/day/Kg MLVSS	0.16		0.16	
Lime Dose,* mg/l (Days 186-212)	52		144	
Lime Dose,** mg/l (Days 213-265)	44		120	
Total Solids Production, mg/l	59.2		97.6	
Total Solids Production, lb/MG	493		813	
Percent of Solids Production in Effluent, %	11.7		9.1	

* Chemstone Hydrated Chemical Grade Lime (9)
** Warner High Calcium Lime

TABLE 12. INFLUENT AND EFFLUENT CHARACTERISTICS FOR THE AIR AND OXYGEN NITRIFICATION SYSTEMS WITH pH CONTROL (DAYS 186-265, 1974)

	Influent, mg/l			Oxygen Nitrification Effluent, mg/l			Air Nitrification Effluent, mg/l		
	Mean	Standard Deviation	Standard Error	Mean	Standard Deviation	Standard Error	Mean	Standard Deviation	Standard Error
BOD_5	56	11.9	1.4	8.8	3.6	0.41	10.4	6.2	0.71
Inhibited BOD_5	--			3.5	1.1	0.13	3.4	1.3	0.15
COD	130	18.6	2.2	20.6	2.6	0.30	20.6	3.4	0.38
SS	65	15.5	1.8	8.1	2.6	0.29	6.2	3.4	0.39
VSS	49	13.1	1.5	4.8	2.1	0.24	4.2	2.5	0.28
TKN	19.5	2.8	0.34	0.94	0.23	0.03	1.0	0.30	0.04
NH_4-N	15.2	2.4	0.28	0.19	0.20	0.02	0.19	0.16	0.02
$(NO_2 + NO_3)$-N	--			13.6	1.2	0.13	12.5	1.2	0.14
Phosphorus	5.4	0.7	0.1	3.4	0.6	0.1	4.0	0.5	0.1

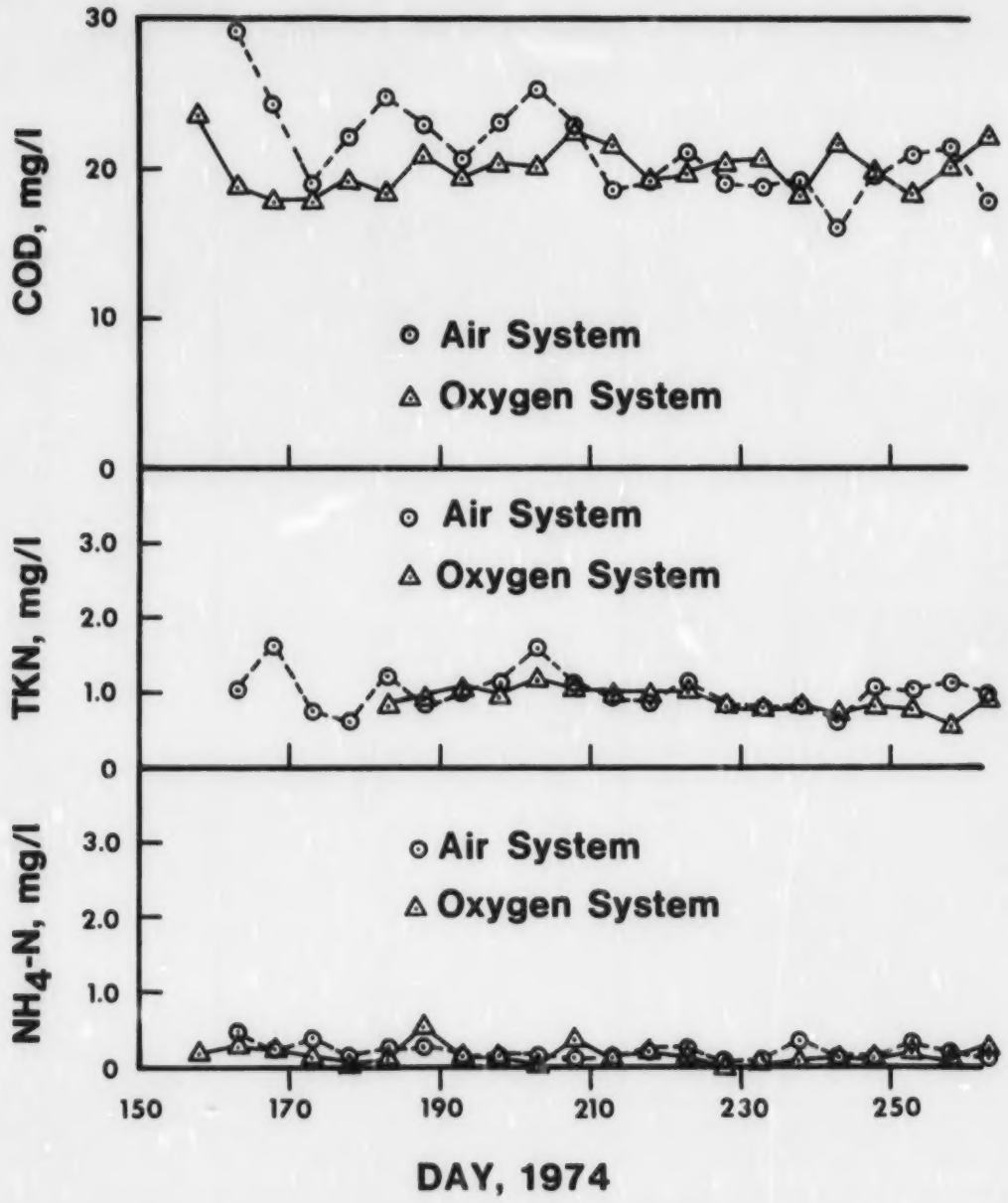

Figure 9. Effluent COD, TKN and NH_4-N for the Air and Oxygen Nitrification Systems (Days 155-265, 1974).

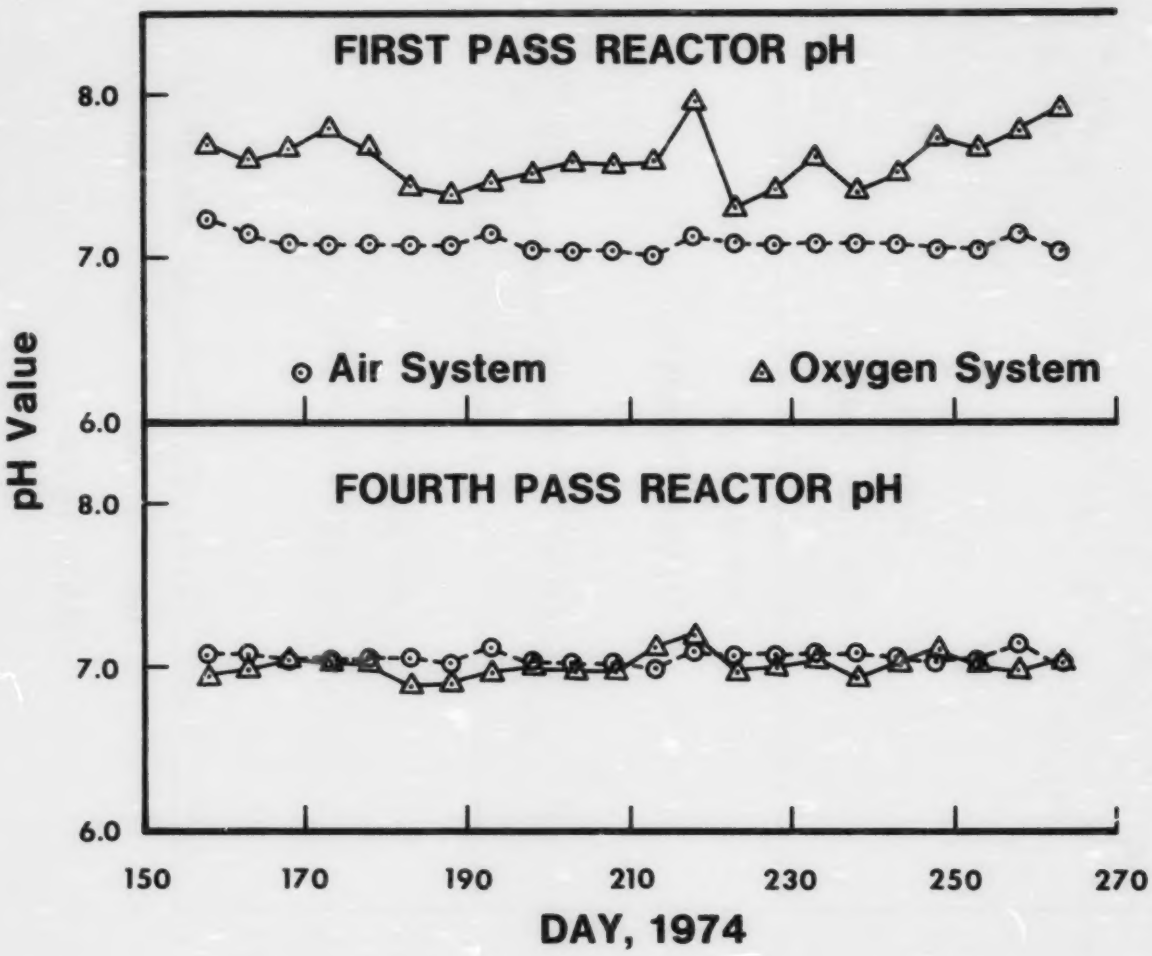

Figure 10. Reactor pH Values for the Air and Oxygen Nitrification Systems (Days 155-265, 1974).

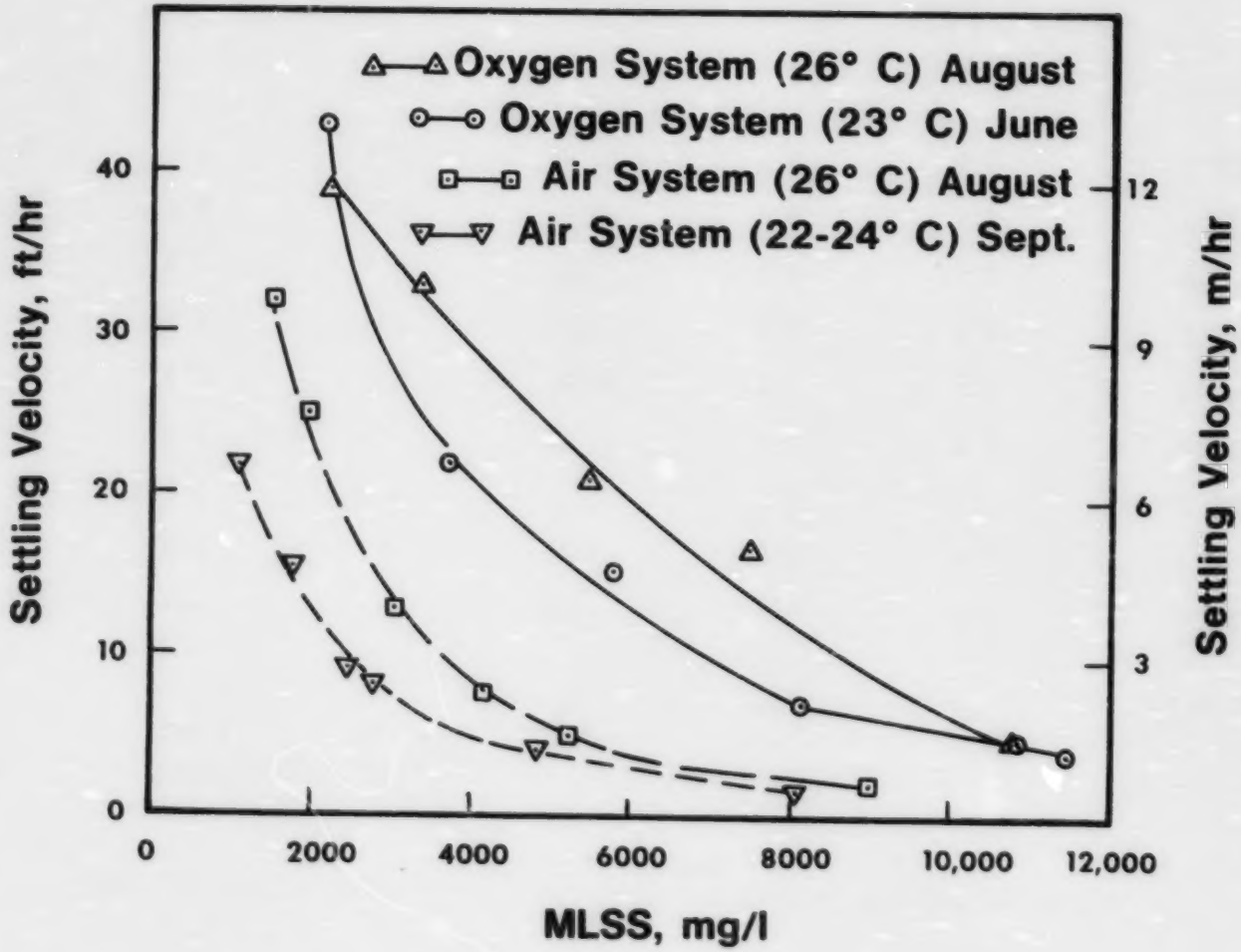

Figure 11. Settling Velocities of Air and Oxygen Nitrification Solids as a Function of MLSS Concentrations.

TABLE 13. NITRIFICATION KINETIC VALUES FOR THE OXYGEN NITRIFICATION SYSTEM WITHOUT pH CONTROL

Date	Median Process pH		Kinetic Study			Kinetic Rate
	Pass 1	Pass 4	Temp. ^{o}C	Initial pH	Final pH	Kg NH_4-N/day / Kg MLVSS
Oct. 25	---	---	20°	---	6.7	0.065
Nov. 15	6.2	5.8	17.5°	6.6	6.6	0.049
Nov. 19	6.0	5.8	19°	6.6	---	0.056
Nov. 30	6.1	5.6	19.5°	6.7	6.4	0.047
Dec. 11	6.2	5.9	18.5°	6.6	6.4	0.042
Dec. 14	6.3	5.9	16°	6.6	6.2	0.029
Dec. 20	6.2	5.9	15°	6.4	6.3	0.027
Jan. 2	5.9	5.3	15.5°	6.6	5.5	0.030
Jan. 15	5.7	5.3	16.8°	6.6	5.5	0.039

TABLE 14. COMPARISON OF THE KINETIC RATES FOR THE OXYGEN NITRIFICATION SYSTEMS WITH AND WITHOUT pH CONTROL

Date	Temp	Kinetic Rates		Kinetic Rate Difference
	°C	Kg NH_4-N/day/Kg MLVSS		$\left[\frac{(A)-(B)}{(B)}\right]$ 100
		Without pH Control (A)	With pH Control (B)	%
Feb 1	17	0.064	0.053	17.1
15	15	0.059	0.047	20.3
26	15.5	0.071	0.060	15.5
Mar 5*	17-17.5	0.116	---	---
5	17-17.5	0.103	---	---
6*	16.5-17	0.094	---	---
6	16.5-17	0.107	---	---
7*	17.5-18	---	0.062	---
7	17.5-18	---	0.063	---
Mar 22*	16.5-17	0.088	0.071	19.3
28*	17.0	0.114	0.065	43.0
Apr 19	19.5	0.094	0.079	16.0
24	19.5-20	0.110	0.070	36.4
30	22.0	0.146	0.103	29.5
May 7	21-22	0.116	0.104	10.3
10	21.0	0.126	0.100	26.0
16	23.0	0.144	0.109	24.3
21	22.0	0.113	0.088	22.1
			Average	23.3

* Period of equal loading to both processes

TABLE 15. COMPARISON OF THE KINETIC RATES FOR THE OXYGEN NITRIFICATION SYSTEMS WITH AND WITHOUT pH CONTROL ON THE BASIS OF MLVSS, PROTEIN AND ATP

Date	System	Temp. °C	MLVSS mg/l	ATP mg/l	Protein mg/l	NH_4-N Removal Rate mg/l/hr	Kinetic Rates: Kg NH_4-N/day / Kg MLVSS	Kinetic Rates: NH_4-N mg/hr / mg ATP	Kinetic Rates: NH_4-N mg/hr / gm protein
4/30	NpH*	22	971	9.3×10^{-2}	---	5.93	0.146	63.8	----
	WpH**	22	2100	6.75×10^{-2}	---	9.00	0.103	133	----
5/7	NpH	21-22	1276	9.1×10^{-2}	701	6.19	0.116	68.0	8.8
	WpH	21-22	1939	5.0×10^{-2}	981	8.40	0.104	168	8.6
5/10	NpH	21	1080	8.1×10^{-2}	540	5.67	0.126	70.0	10.5
	WpH	21	1410	3.4×10^{-2}	---	5.87	0.100	173	----
5/16	NpH	23	1160	9.0×10^{-2}	574	6.98	0.144	77.6	12.2
	WpH	23	2335	5.3×10^{-2}	1115	10.58	0.109	199	9.5
5/21	NpH	22	779	----	426	3.67	0.113	----	8.6
	WpH	22	1890	----	851	6.90	0.088	----	8.1

* NpH (no pH control)
** WpH (with pH control)

TABLE 16. EFFECT OF pH ON NITRIFICATION KINETIC RATE
FROM THE OXYGEN SYSTEM
WITHOUT pH CONTROL

Date	Temp. ^{o}C	Kinetic Study		Kinetic Rate Kg NH_4-N/day / Kg MLVSS
		Initial pH	Final pH	
Nov. 15*	17.5	6.6	6.65	0.049
Nov. 16	18.5	7.5±0.1	7.5±0.1	0.048
Nov. 20	19	7.3±0.2	7.3±0.2	0.048
Jan. 16	17	6.6±0.1	6.6±0.1	0.038
Jan. 16	17	5.8±0.1	5.8±0.1	0.032
Feb. 28	15	6.1±0.05	6.1±0.05	0.091
Feb. 28	15	5.5±0.02	5.5±0.02	0.057
April 4	17.5-18	5.9±0.05	5.9±0.05	0.135
April 4	17.5-18	5.6±0.05	5.6±0.05	0.120
April 4	17.5-18	5.5±0.05	5.5±0.05	0.114
April 4*	17.5-18	6.6	5.9	0.139

* pH not controlled

TABLE 17. SUSPENDED SOLIDS CONCENTRATIONS AND NH_4-N FOR THE OXYGEN NITRIFICATION SYSTEM WITHOUT pH CONTROL

(Day 94 - April 4, 1974)

Time	NH_4-N Concentration, mg/l					Suspended Solids, mg/l			
	Influent	Pass No. 1	Pass No. 2	Pass No. 3	Pass No. 4	Pass No. 1	Pass No. 2	Pass No. 3	Pass No. 4
0850	10.95								
0900						2000		1780	
0945	11.20								
1030	11.15	1.55							
1045							1940		1785
1130	10.95	2.10	0.40						
1145						2140		1895	
1315	11.50	2.0	0.40						
1345						1950	1905		
1400				0.20	0.15				
1450	11.60	2.25	0.40						
1530						1905	1790		
1650	12.70	2.50	0.60	0.20					

TABLE 18. SUMMARY OF AIR AND OXYGEN NITRIFICATION SYSTEM KINETIC STUDIES

Date	System	Temp. °C	MLVSS mg/l	Protein mg/l	NH_4-N Removal Rate mg/l/hr	Kinetic Rates: Kg NH_4-N/day / Kg MLVSS	Kinetic Rates: mg NH_4-N/hr / gm protein
06-20	Air	23.5	1640	760	8.16	0.120	10.7
	Oxygen		2545	1195	10.1	0.095	8.45
06-28	Air	23.0	1325	610	6.94	0.126	11.4
	Oxygen		1775	825	7.60	0.103	9.21
07-02	Air	24.5	1375	670	9.16	0.160	13.7
	Oxygen		1710	640	9.10	0.128	14.2
07-11	Air	26.0	1355	675	8.18	0.145	12.1
	Oxygen		1665	935	11.9	0.171	12.7
07-16	Air	26.0	1500	690	9.47	0.151	13.7
	Oxygen		2040	965	13.7	0.161	14.2
07-26	Air	26.0	1395	705	9.36	0.161	13.3
	Oxygen		1555	795	11.3	0.174	14.2
08-02	Air	25.0	1095	480	6.15	0.135	12.8
	Oxygen		1420	815	8.70	0.147	10.7
08-09	Air	25.0	1385	---	7.70	0.133	----
	Oxygen		1655	---	10.5	0.152	----

TABLE 18
(Continued)

Date	System	Temp. °C	MLVSS mg/l	Protein mg/l	NH_4-N Removal Rate mg/l/hr	Kinetic Rates: Kg NH_4-N/day / Kg MLVSS	Kinetic Rates: mg NH_4-N/hr / gm protein
08-15	Air	27.0	1165	630	6.0	0.124	9.52
	Oxygen		1740	900	11.8	0.163	13.1
08-23	Air	26.0	1165	---	4.77	0.098	----
	Oxygen		1545	---	9.35	0.145	----
09-05	Air	23.0	1000	505	3.84	0.092	7.60
	Oxygen		1845	983	9.77	0.127	9.94
09-11	Air	24.5	1230	625	6.60	0.129	10.6
	Oxygen		1790	1011	10.3	0.138	10.2
09-24	Air	24.5	1380	753	9.43	0.164	12.5
	Oxygen		1760	1043	10.5	0.144	10.1

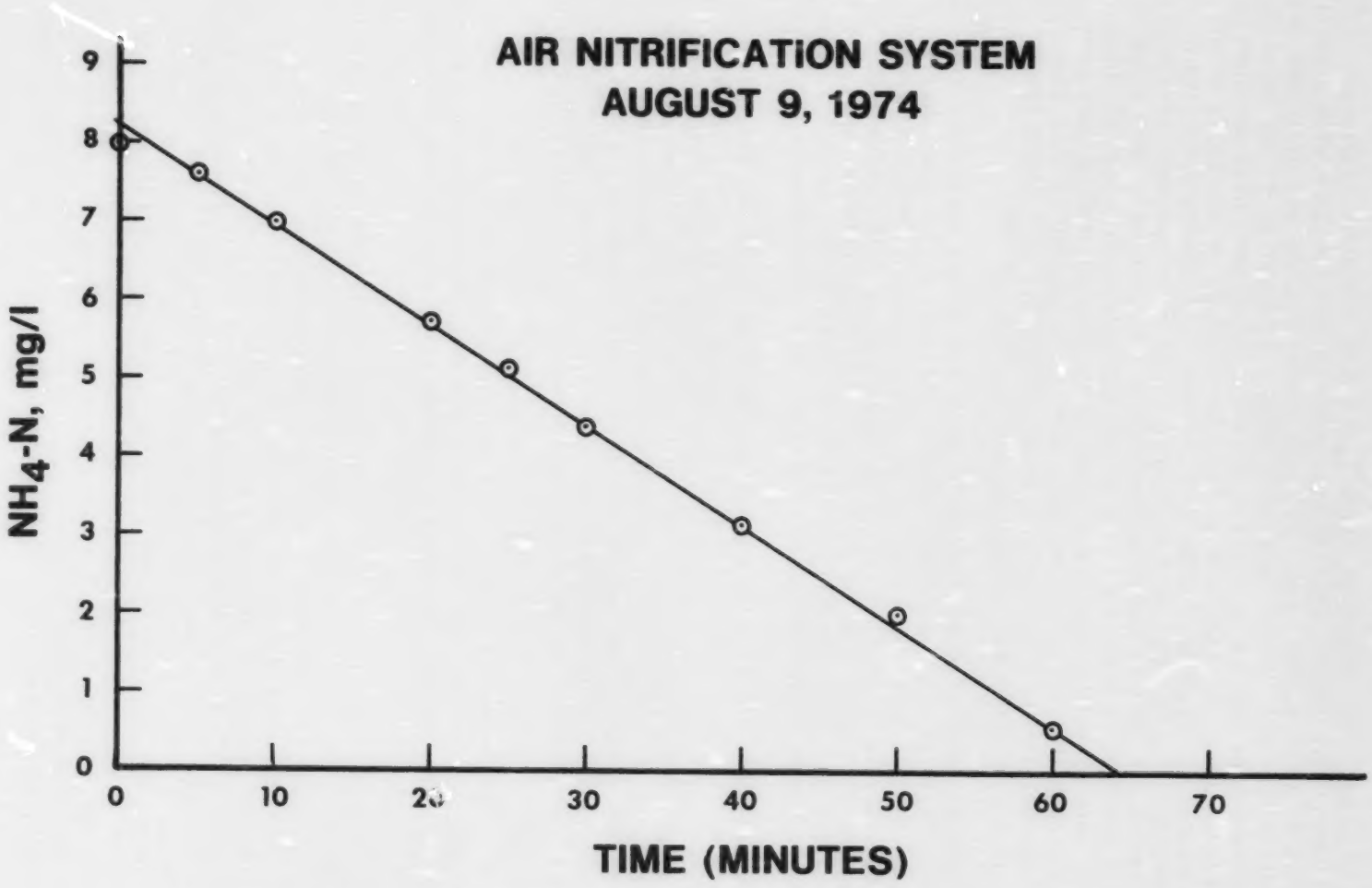

Figure 12. Laboratory Determination of Nitrification Kinetic Rate.

the basis of MLVSS. The values on March 5, 6 and 7 represent duplicate studies in which pure oxygen aeration was compared with aeration with a small portion of the actual process gas. It is apparent that the use of oxygen in the laboratory does not affect the kinetic rate. In addition to the volatile solids determination the sludge protein and ATP content were also measured in a few selected cases. A comparison of the kinetic rates on the basis of all three parameters is presented in Table 15. There is no consistent pattern with respect to the rates per unit of protein. The rates per unit of ATP were considerably higher in the pH controlled system. However, this difference is difficult to interpret because of the differing F/M ratios at which the systems were operating when these comparative kinetic studies were performed. Although the influent flow rates were quite similar at this time, the MLVSS concentration in the system without pH control was approximately half that in the pH controlled system (Figure 6, days 100-140).

A few laboratory batch kinetic studies in which the pH was controlled are presented in Table 16. Although the number of studies is limited, they do provide some insight into the effect of pH on a system acclimated to low pH conditions. Above a pH of 6.0-6.1, there appears to be little advantage in increasing the pH. Below a pH of 6, there is a decline in the kinetic rate with decreasing pH. Considerable nitrification still occurs at pH 5.5. How low the pH can be reduced before nitrification ceases is unknown.

The values presented in Table 16 for day 94 (April 4) represent the result of a series of studies to confirm that the laboratory kinetic studies are representative of actual process potential. The value for uncontrolled pH was determined in the laboratory in the normal manner, i.e. oxygen aeration with no pH control. The three additional kinetic values reported were obtained in the following manner. A sample of mixed liquor from a given reactor pass was withdrawn and the pH was carefully measured. Next NH_4Cl was added to the sample to produce an NH_4-N concentration of about 10 mg/l. The sample was then aerated with a portion of the gas stream that was being used for that particular pass in the actual process. Lime was added as required to maintain the pH within ±0.05 pH units of the initial pH. The kinetic rate at pH 5.9 was the same as that measured in the laboratory kinetic test with oxygen aeration. The kinetic rate declined with further decreases in pH.

Samples of process influent and of reactor mixed liquor were analyzed throughout the day that the above mentioned studies were performed. The results are presented in Table 17. Influent flow during this period was 143.5 l/min (37.9 gpm) and the recycle flow was 49.6 l/min (13.1 gpm) yielding a total flow through the process of 193.1 l/min (51.0 gpm). Each reactor pass has a volume of 7.65 m^3 (2020 gal) yielding a detention time of 0.66 hours at the 193 l/min (51 gpm) total flow. The soluble NH_4-N concentration of the recycle flow was 1.1 mg/l. Using the average of all NH_4-N concentrations measured in the influent and in the first pass, the average influent NH_4-N concentration (proportioned to include mixing with recycle) was 8.78 mg/l and the average Pass No. 1 NH_4-N concentration was 2.08 mg/l. Average solids were 2000 mg/l and were 84.4% volatile. By treating the first pass as a completely mixed, continuous flow reactor with no backmixing, the kinetic rate

for NH_4-N removal was 0.144 gm NH_4-N/day/gm MLVSS. When using those values between 0850 hours and 1450 hours (which corresponds to the period of steady influent NH_4-N) the kinetic rate is 0.141 gm NH_4-N/day/gm MLVSS. It can be seen that this kinetic rate (0.141) is essentially the same as shown in Table 16 for the kinetics test with Pass No. 1 (0.135) or that obtained in the regular kinetics test (0.139). The process kinetic rate determined by the difference in influent and Pass No. 1 values could be biased slightly toward the high side because of a small amount of backmixing with the second pass of the reactor. However, this is not felt to be significant.

Observation of the results of all the batch kinetics tests indicates that the NH_4-N removal rate in short-term studies is independent of exogenous NH_4-N concentrations above a concentration of about 1 mg/l. Hence, the rate measured in Pass No. 1 is concentration independent. This is not the case, however, for the kinetic rate in the second pass. Using the average of all values for Pass No. 1 and Pass No. 2 and treating Pass No. 2 as an ideal complete mix reactor, yields an NH_4-N removal of 1.63 mg/l and a kinetic rate of 0.037 gm NH_4-N/day/gm/MLVSS. This kinetic rate is only 26% of that rate measured in the first pass and reflects the change from a concentration independent kinetic rate to a concentration dependent rate. The kinetic tests at various pH values indicate that the main factor is truly concentration with the lower pH playing a minor role (in the pH ranges explored in this study). Examination of the concentrations reported for Passes 3 and 4 reveals a continuing decline in kinetic rate as the concentration decreases. This is exactly what is expected.

Since the air and oxygen nitrification systems were operated under similar loading conditions throughout the period when their performance was being compared, their kinetic rates can be directly compared in a more meaningful way. The kinetic rates obtained during this period of operation are summarized in Table 18. The protein concentrations, as estimated by the Folin Procedure, were a constant percentage of the MLVSS within both systems (Table 19). In all cases the kinetic rates were similar on any given day. Furthermore there was no tendency for either of the systems to have kinetic rates consistently higher or lower than the other.

On several occasions during the study, the mixed liquor from the fourth pass of the systems was removed for a determination of the settling velocity in the 0.15 m (6 inch) column. The results of these determinations are summarized in Table 20. The lime addition caused a large amount of non-volatile material to be carried in the oxygen system with pH control. For example, the average mixed liquor volatile solids concentration in this system for days 186-265 was only 36%. Hence high MLSS concentrations were necessary to maintain the MLVSS concentrations desired. Nevertheless, the increased settling velocity resulting from the lime addition compensated for the higher MLSS levels which were needed in the pH controlled oxygen system compared to the levels in the air nitrification system with pH control (average MLVSS concentration of 58% from days 186-265) or the oxygen system with no pH control.

On a few occasions during the study, the oxygen uptake rates in the oxygen or air system were measured. These rates are summarized in Table 21. The lower than normal rates on July 31 reflect the presence of storm water in the wastewater.

TABLE 19. SUMMARY OF MLVSS
AND
PROTEIN VALUES FOR SELECTED KINETIC TESTS

DATE	AIR NITRIFICATION SYSTEM			OXYGEN NITRIFICATION SYSTEM		
	MLVSS mg/l	PROTEIN mg/l	% PROTEIN	MLVSS mg/l	PROTEIN mg/l	% PROTEIN
6/20	1640	760	46.3	2545	1195	47.0
6/28	1325	610	46.0	1775	825	46.5
7/2	1375	670	48.7	1710	640	37.4
7/11	1355	675	49.8	1665	935	56.1
7/16	1500	690	46.0	2040	965	47.3
7/26	1395	705	50.5	1555	795	51.1
8/2	1095	480	43.8	1420	815	57.4
8/15	1165	630	54.1	1740	900	51.7
9/5	1000	505	50.5	1845	983	53.5
9/11	1230	625	50.8	1790	1011	56.5
9/24	1380	753	54.6	1760	1043	59.3

TABLE 20. MIXED LIQUOR SUSPENDED SOLIDS SETTLING VELOCITIES FOR THE AIR AND OXYGEN NITRIFICATION SYSTEMS

Month	Oxygen Nitrification System Without pH Control (March-April) and Air Nitrification System				Oxygen Nitrification System With pH Control			
	Temp °C	MLSS mg/l	Settling Velocity ft/hr	Settling Velocity m/hr	Temp °C	MLSS mg/l	Settling Velocity ft/hr	Settling Velocity m/hr
March	16.5	3200	12.5	3.8	17.5	5000	14.3	4.4
	17.5	3200	11.4	3.5	17.5	5100	14.1	4.3
	17.5	3000	12.3	3.7	17.5	5100	11.7	3.6
April	17.0	2000	15.0	4.6	17.5	5200	11.9	3.6
					17.5	4200	11.6	3.5
					20.0	6500	9.4	2.9
					21.5	6900	9.6	2.9
May					22.0	6900	15.9	4.8
					23.0	7400	10.0	3.0
June	24.0	4500	7.8	2.4	23.0	5000	16.8	5.1
					24.0	6500	10.9	3.3
					24.0	6400	10.6	3.2
July	26.5	4600	6.9	2.1	26.5	6300	6.6	2.0
	26.5	3900	7.7	2.3	26.5	5300	9.1	2.8
August	27.0	4100	8.6	2.6	27.0	7100	9.7	3.0
	27.0	4000	6.8	2.1	27.0	8400	9.7	3.0
	27.0	4500	8.8	2.7				
September	25.0	3700	6.8	2.1	24.0	5400	12.4	3.8
	26.0	3900	7.6	2.3	25.0	5800	12.9	3.9
	25.0	3600	6.4	2.0				
	23.0	2800	9.0	2.7				

TABLE 21. OXYGEN UPTAKE VALUES FOR SELECTED GRAB SAMPLES WITH THE OXYGEN AND AIR NITRIFICATION SYSTEMS

Date 1974	Pass No.	Oxygen Nitrification Systems				Air Nitrification System	
		With pH Control		Without pH Control		With pH Control	
		mg/l/hr	mg/hr / gm MLVSS	mg/l/hr	mg/hr / gm MLVSS	mg/l/hr	mg/hr / gm MLVSS
March 1	1	62	23	60.5	22		
	2	25	9	36	12		
	3	23	8.4	37	13		
	4	19	7	17	6		
April 17	1	34.8	27.5	57	22.7		
	2	28.0	25.0	22.0	8.8		
	3	23.4	19.6	18.0	7.2		
	4	16.5	13.5	17.1	6.9		
May 9	1	39	27.0	48	22.7		
	2	37.7	26.5	12.6	8.7		
	3	20.4	15.3	12.0	6.0		
	4	16.5	11.8	12.2	4.4		
May 20	1	34.8	29.6	60	22.1		
	2	30.0	27.8	20.4	7.6		
	3	19.3	14.7	16.5	6.3		
	4	14.6	11.5	16.8	6.3		
July 31	1	26.7	10.9			25.0	10.8
	2	15.8	7.0			20.8	8.8
	3	17.5	7.6			23.5	9.9
	4	15.3	6.5			21.2	9.2

SECTION VIII

DISCUSSION

The effluent NH_4-N levels from the oxygen nitrification system with pH control were extremely low throughout the period of study. By comparison, the oxygen system without pH control did not exhibit the same stability (e.g. Figure 4, Days 30-50) and the residual NH_4-N levels tended to run somewhat higher. Yet even without the pH control, the NH_4-N level was normally 1 mg/l or less. Also good recovery of nitrification was experienced with this system after the loss of a large portion of the solids due to a mechanical failure at the end of March.

To achieve pH control at 7.0 in the last pass required a lime dose of about 125 mg/l. This resulted in considerably more inorganic sludge production than in the process with no pH control and a 50 mg/l increase in calcium ion in the process effluent.

It is apparent that the nitrifying organisms can acclimate to and function well at relatively low pH values. Haug and McCarty (10) found good growth at pH 6.0 following a suitable period of acclimation. Similarly, Stankewich (11) observed consistent nitrification in his oxygen nitrification studies at a pH of 5.8-6.0. For the oxygen system with no pH control in this study, the normal range in reactor pH was from 5.5-6.0. It was not uncommon for the pH in the last pass to fall to 5.3. Nitrification still occurred at these pH values although the data in Table 16 do show that the kinetic rate starts declining below a pH of 5.9-6.0 even in a system acclimated to lower pH conditions. Additional studies to more carefully define the nitrification rate as a function of pH would be of interest. At this time it would appear that if pH control is to be employed in an oxygen system to insure the degree of stability that was attained in this study with pH control, one could probably maintain a pH of just 6.0 in the final pass with no detrimental effects on the nitrification rate.

The cell yield coefficients for Nitrosomonas and Nitrobacter reported in the literature are variable. Poduska (12) summarized reported values and concluded that using 0.05 gm Nitrosomonas formed per gm NH_4-N oxidized and 0.02 gm Nitrobacter formed per gm NO_2-N oxidized were reasonable estimates of sludge yield. Lawrence and Brown (13) using the estimates of Downing et. al. (14) also utilized the above mentioned yield coefficients in their kinetic evaluations.

Using an influent NH_4-N concentration of 16 mg/l as being typical of Blue Plains secondary effluent and neglecting that fraction of the NH_4-N or organic nitrogen metabolized into carbonaceous organisms, produces a daily

yield of nitrifying organisms of roughly 212 gm/day [(50,000)(3.785)(16)(0.07)(10^{-3})]. Using a conservative estimate of carbonaceous sludge production of 0.35 gm solids/gm of BOD_5 applied yields a daily carbonaceous sludge production with a 65 mg/l influent BOD_5 of 4305 gm/day [(50,000)(3.785)(65)(0.35)(10^{-3})]. This corresponds to a sludge production of 22.8 mg/l (190 lb/MG). The sludge production value reported in Table 1 for high SRT operation and similar loading conditions was also 22.8 mg/l (190 lb/MG). In this case the nitrifying organisms would comprise only 4.7 per cent of the total cell population. While these numbers can be altered by including cell maintenance coefficients, correcting for nitrogen metabolized into carbonaceous organisms or organic nitrogen converted to ammonia, etc., the basic point which must be considered is that the nitrifying organisms comprise a very small percentage of the sludge mixed liquor. Hence, for this study, when the kinetic rates are evaluated per unit of MLVSS or per unit of protein, the rates are actually being expressed almost entirely as a function of the mass of carbonaceous organisms present. So long as this is clearly understood, the evaluation of nitrification kinetic rates per unit of MLVSS or protein can provide valuable insights into system performance. However the direct comparison of nitrification kinetic rates per unit of system mass between systems receiving different influent wastewaters or even between systems receiving the same influent wastewater but operated under different conditions can lead to erroneous conclusions unless all variables impacting on total system mass as well as the variables affecting the nitrification rate per unit of nitrifying organisms are considered.

The kinetic rates reported in Table 14 show that the nitrification kinetic rates obtained in the laboratory were consistently somewhat higher for the oxygen nitrification sludge in the system with no pH control. However the differences are small and could easily reflect other factors not related to nitrification, eg. different predominating heterotrophic populations because of the difference in pH with slightly different yield coefficients. The kinetic rates give no evidence that operation at the uncontrolled pH ranges observed in this study is detrimental to the development of a nitrifying population with capabilities equivalent to that from the pH controlled system. Obviously the response of any particular process will depend on the rate decline as a function of pH (as illustrated in Table 16) in conjunction with the excess capacity of the process for complete nitrification as described in Table 17. In this case (Table 17), the rate decline which occurs in the fourth pass because of the lower pH is overshadowed by the low rate resulting from the very low residual NH_4-N concentration. This relationship of residual NH_4-N and substrate removal is predicted by Monod kinetics and has been discussed by a number of authors previously.

The oxygen nitrification system with pH control was not operated at widely varying F/M loadings during the study. Since pH was also controlled. the major factor affecting the nitrification kinetic rate was the process temperature. The laboratory batch kinetic rates are presented as a function of temperature in Figure 13. Both the linear and exponential regression equations are presented. It can be seen that an excellent correlation was obtained.

As indicated in Table 12, there was no difference in carbonaceous or nitrogenous effluent quality when parallel air and oxygen systems were examined.

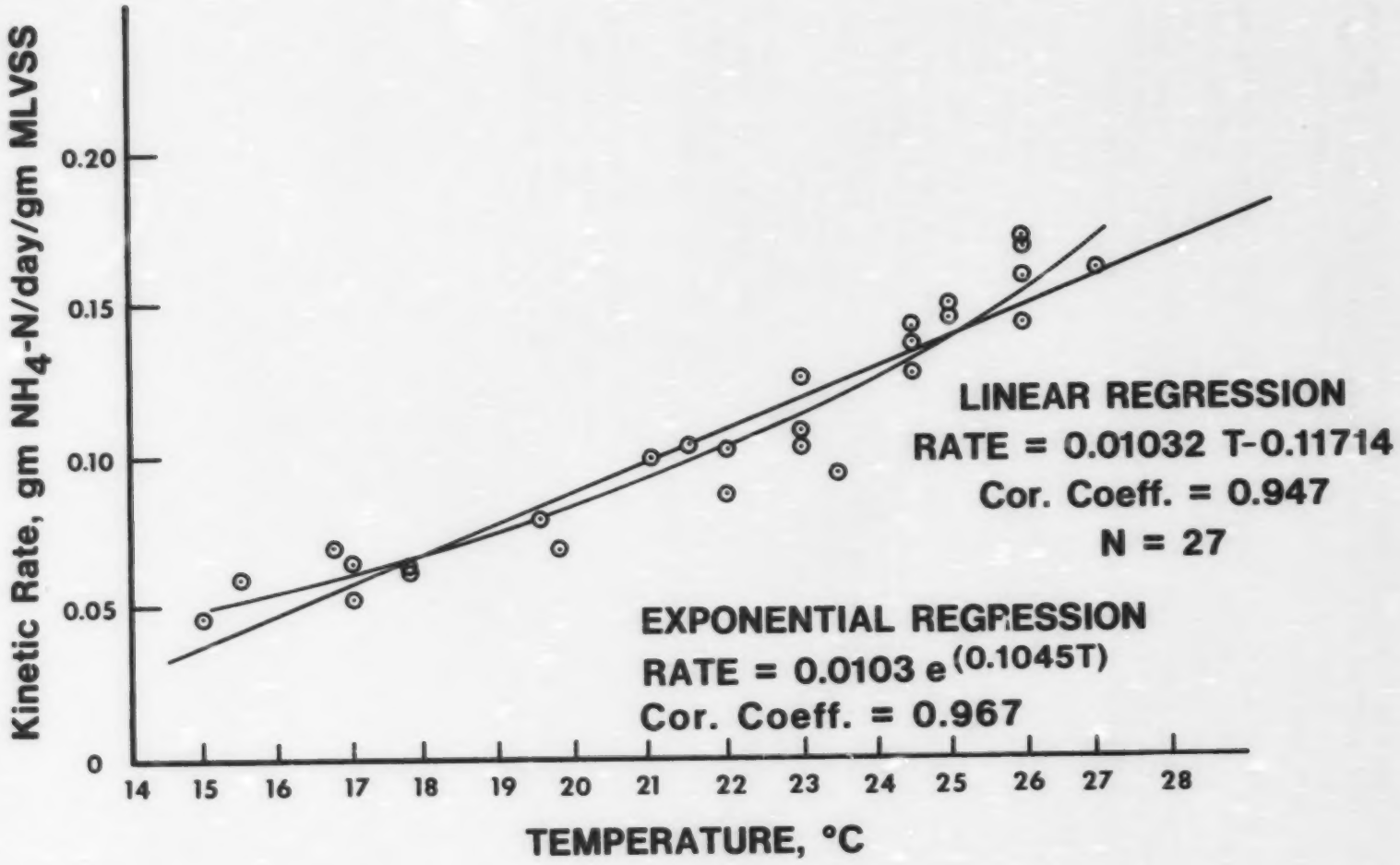

Figure 13. Nitrification Kinetic Rate vs Temperature for the Oxygen Nitrification System With pH Control.

Similarly as shown in Table 18, the kinetic rates were essentially the same. The sludge yield coefficients and decay coefficients were reported by Humineck and Ball (15) to be essentially the same under aeration or oxygenation. Others (16) have questioned this conclusion.

A total of 24 dissolved oxygen readings were taken daily in each of the two nitrification systems, and the average daily levels are shown in Figure 14. The mean D.O. level in the air system was 3.0 mg/l. The mean level in the oxygen system was 8.1 mg/l, but the variation was considerably larger than encountered in the air system. However, the mean D.O. in the oxygen system was less than 6 mg/l on just 7 of the 80 days under consideration here.

The assumption of equal yields and equal decay coefficients during the period of parallel operation of the air and oxygen systems is firmly supported by the volatile solids sludge production data and the calculated net oxygen utilization. Although the total solids production reported in Table 11 is substantially higher for the oxygen system, this is due to the greater lime dosage. The total production of volatile suspended solids was 34.6 mg/l for the air system and 35.5 mg/l for the oxygen system. This difference of just 2.6 per cent is negligible and well within experimental error. The systems can also be compared by calculating the oxygen utilization based on the COD and (NO_2 + NO_3)-N data. Grab samples of effluent from both systems were periodically analyzed for NO_2-N, but none was ever found. Hence the reported (NO_2 + NO_3)-N effluent values are actually NO_3-N. The net oxygen demand of each system was calculated as shown in Table 22. Again it can be seen that the difference between the two values is only 1.9 per cent which is well within experimental error. These data indicate that the kinetic rates per unit of protein or VSS reported in Table 18 should be directly comparable.

Maintaining the last pass of the oxygen and air systems at pH 7.0 required nearly 3 times the lime dosage in the oxygen system. This apparently was responsible for the slightly enhanced phosphorus removals. The large lime dosage did result in a better settling sludge with a much lower average SVI. It, of course, also resulted in much higher sludge production.

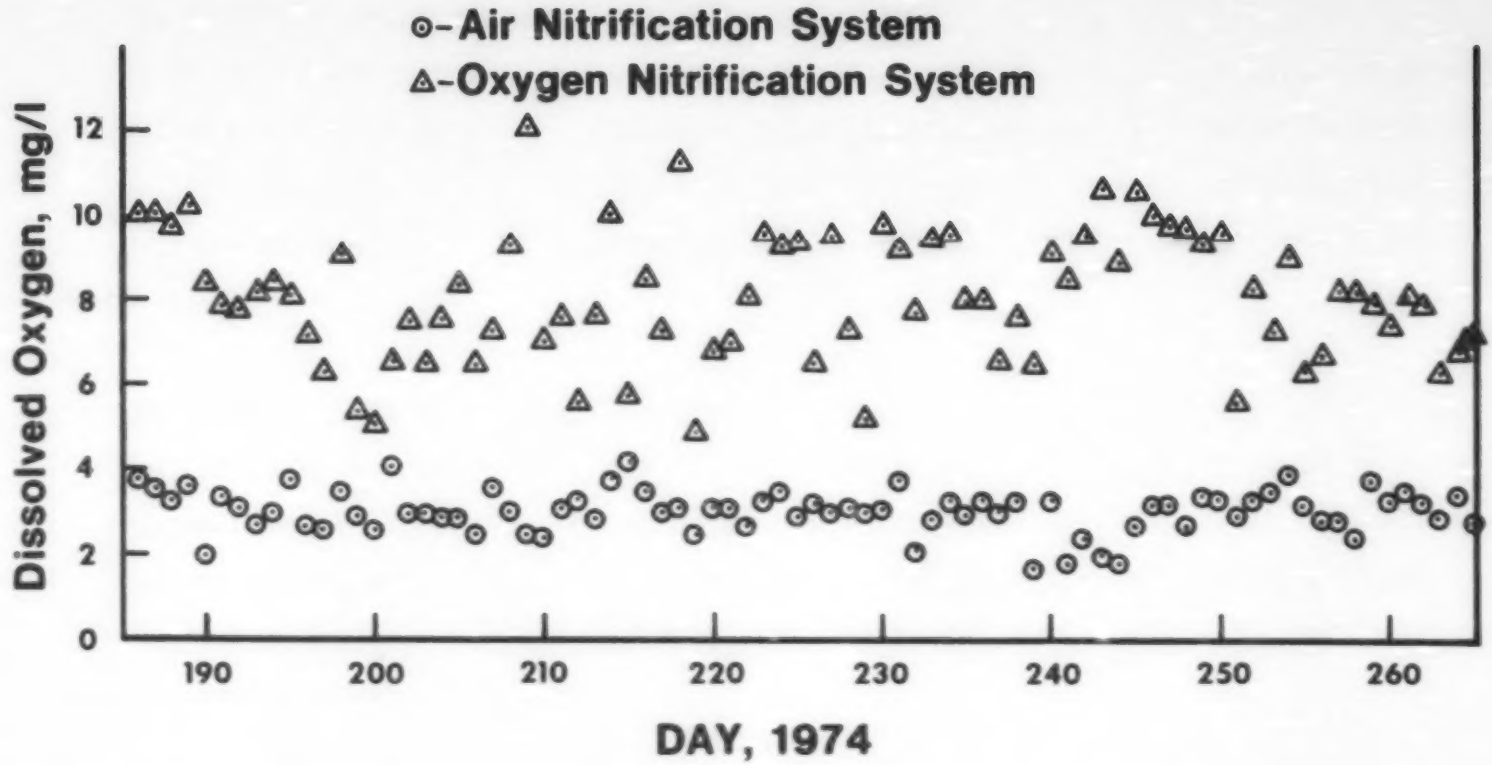

Figure 14. Average Daily Dissolved Oxygen Concentrations in the Air and Oxygen Nitrification Systems (Days 186-265, 1974).

TABLE 22. A COMPARISON OF OXYGEN CONSUMPTION IN THE AIR AND OXYGEN NITRIFICATION SYSTEMS WITH pH CONTROL

(DAYS 186-265, 1974)

Air Nitrification System:

Influent COD x Flow	$(130)(10^{-3})(52,900)(3.785)$	=	26,030 gm O_2/day
Effluent COD x Flow	$(20.6)(10^{-3})(52,700)(3.785)$	=	4,110 gm O_2/day
Effluent (NO_3)-O_2 x Flow	$(12.5)(48/14)(10^{-3})(52,700)(3.785)$	=	8,550 gm O_2/day
Waste COD x Waste Flow	$(13,050)(10^{-3})(170)(3.785)$	=	8,400 gm O_2/day

Net Oxygen Utilization : 22,070 gm O_2/day

Oxygen Nitrification System:

Influent COD x Flow	$(130)(10^{-3})(51,200)(3.785)$	=	25,190 gm O_2/day
Effluent COD x Flow	$(20.6)(10^{-3})(51,100)(3.785)$	=	3,980 gm O_2/day
Effluent (NO_3)-O_2 x Flow	$(13.6)(48/14)(10^{-3})(51,100)(3.785)$	=	9,020 gm O_2/day
Waste COD x Waste Flow	$(18,240)(10^{-3})(112)(3.785)$	=	7,730 gm O_2/day

Net Oxygen Utilization : 22,500 gm O_2/day

SECTION IX

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7. Defined as (MLVSS)(Reactor Volume) - [(Waste VSS)(Waste Flow) + (Effluent VSS)(Process Flow)].

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9. Chemstone Hydrated Chemical Grade Lime is stated by the manufacturer to have an equivalent minimum CaO content of 72%.

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